University of Alberta

The use of constructed wetlands to treat oil sands wastewater, Fort McMurray, Alberta, Canada.

by

Farida Susanne Bishay ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science.

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled The Use of Constructed Wetlands to Treat Oil Sands Wastewater, Fort McMurray, Alberta, submitted by Farida Susanne Bishay in partial fulfillment of the requirements for the degree of Master of Science in Environmental Biology and Ecology.

Suzanne Bayley, Ph.D.

Michael Hickman, Ph.D.

William McGill, Ph.D.

Dedicated To

Daddy, Assaad Bishay (1935-1977)
Mormor, Asta Schaltz (1898-1993)
Auntie Nadia, Nadia Bishay (1927-1995)
Uncle Samy, Samy Bishay (1935-1996)

They taught me that
to run is to discover,
to remember is to understand,
to teach is to learn,
and to write is to share.

ABSTRACT

Constructed wetlands are a component of the mine reclamation plan for Suncor Inc., Oil Sands Group, a large oil sands mining and extraction operation in northeastern Alberta, Canada. Over a three year period (1992 - 1994), the feasibility of constructed wetlands as treatment systems for various oil sands wastewater streams was assessed. The removal rates of ammonia and hydrocarbon, the primary contaminants, were estimated by measuring inputs and outputs, changes in storage, and removal processes. Removal rates ranged from 32 to 99 % and 19 to 76 % for ammonia and hydrocarbons, respectively. Removal rates decreased as input load increased. Loads removed were about 200 mg m^{-2} d^{-1} and 170 mg m^{-2} d^{-1} for ammonia and hydrocarbons, respectively (on average during the period of wastewater application). Measurements of storage and transformation processes suggested the dominant fate pathways were sediment retention and nitrification/denitrification for ammonia and sediment retention and microbial mineralization for hydrocarbons. Macrophyte production and decomposition were measured to assess viability and sustainability. Production (as measured by peak standing crop) and decomposition (as measured by weight loss) were only significantly different among treatments in 1993 under higher hydraulic loading rates of 4.9 cm/d compared with 1.6 cm/d in 1992 and 1994. Production (mean ± SD) in 1993 was 585 ± 243, 470 ± 175 and 453 ± 216 g/m^2 in Control, Dyke and Pond trenches, respectively. Decomposition (mean ± SD) in 1993 was 52.2 ± 9.1 %, 47.2 ± 4.2 % and 35.6 ± 4.9 % in Control, Dyke and Pond trenches, respectively. The treatment wetlands provided significant contaminant retention under lighter loading, and macrophyte production and decomposition were not impacted at these lighter loadings. However, longer-term, larger-scale demonstrations would be required to determine viability and sustainability of constructed wetlands. Such facilities are currently planned and are considered the next step by the oil sands industry before design and implementation of full scale constructed wetlands.

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1.0 INTRODUCTION

1.1 Suncor and the oil sands extraction process

Suncor Inc., Oil Sands Group (Suncor) is the first of two companies mining oil sands in northeastern Alberta, Canada, 25 km north of Fort McMurray (Figure 1.1). The mining and subsequent conversion of oil sands to synthetic crude oil began in 1967. There are three elements to produce synthetic crude oil: (1) mining of the oil sands; (2) extraction of bitumen (oil) from the sand; (3) upgrading of the bitumen to synthetic crude oil. These three processes and related activities produce various deleterious wastes which are released directly or indirectly (*i.e.*, after some treatment) into the environment.

There are several environmental concerns associated with the production of synthetic crude oil. Mining practices directly alter vegetation patterns (by the removal of spruce and tamarack forests) and the hydrology of the region (by draining land surfaces). Extraction of the bitumen produces fine tailings which are stored in several large tailings ponds (Figure 1.2). The upgrading and power generation processes release pollutants (*e.g.*, SO_2) to the atmosphere.

While all these factors affect the environment, the current study will focus on the problem of the accumulating fine tailings. In the process of extracting bitumen (*i.e.*, the Clark Hot Water Extraction Process) from the oil sands, a waste product called fine tails is produced. Fine tailings are an aqueous suspension of sand, silt, clay and residual bitumen and naphtha with a pH between 8 and 9 (FTFC, 1995a). Fine tailings have been stored in large clay lined tailings ponds to date.

These ponds must be reclaimed to a viable land surface or water body free of long term maintenance (Nix and Martin, 1992). There are two types of reclamation scenarios: dry landscape and wet landscape (Gulley and MacKinnon, 1993). Dry landscape options include amending fine tails with soil or spreading layers of fine tailings over large areas to undergo drying (*i.e.*, evaporation of associated water) in summer and freeze-thawing (*i.e.*, separation of water from clay by freezing and thawing) in winter/spring. The main objective of the dry landscape reclamation plan is to significantly reduce the water content of the fine tailings such that a solid deposit is produced, which could be capped with soil as part of a terrestrial

reclamation plan (FTFC, 1995b). The wet landscape scenario deposits the fine tailings as a fluid requiring geotechnically secure containment. The objective of the wet landscape reclamation plan is to isolate the fine tailings under a layer of water which would act to establish a viable, self-sustaining aquatic system above the fine tailings layer (FTFC, 1995b).

There is a potential for water release from both dry and wet landscape scenarios. Although the water quality of these released waters is expected to be good (FTFC, 1995b), the contaminant load is unknown. To address this potential water release either a collection system must be maintained or a treatment system created. Wetlands would act as a polishing treatment system for water leaving the reclaimed site before entering the receiving environment (Gulley and Klym, 1992).

To meet the demands of a reclamation plan, a wetland treatment system was investigated by Suncor. Two main types of water have been assessed in the experimental constructed wetlands: leachate from saturated tailings pond sand dykes (as a surrogate for all leachate water types) and tailings pond top water (as a worst case scenario). Leachate water (from the tailings pond or precipitation throughfall that has passed through sand dyke walls and coke filters) is currently gravity fed to a pumping station which returns it to the tailings pond (or recycles it through the extraction plant). Water for the constructed wetlands was obtained from this pumping station and will be referred to as Dyke Drainage or Dyke water. Tailings pond water (lower in suspended solids compared with fine tailings, but much higher compared with Dyke water) is decanted from one tailings pond (Pond 1) into another (Pond 1A) containing recycle water only (*i.e.*, no fine tailings). Water for the constructed wetlands was obtained from surface waters of Pond 1A and will be referred to as Pond 1A or Pond water.

Organic (*e.g.*, naphthenic acids) and inorganic (*e.g.*, ammonia) contaminants are of concern in both Dyke and Pond water. Although naphthenic acids exist naturally in bitumen (Fan, 1991) and are not formed during the extraction and refining process (AEP, 1996), there are elevated levels of solubilized naphthenic acids in oil sands fine tailings due to the alkaline hot water extraction processing of oil sands (MacKinnon and Boerger, 1986). Naphthenic acids are present as sodium salts in oil sands wastewater (Herman et al., 1994). The primary source of ammonia is the sour water, which contains both reduced sulphur and ammonia products. Sour water is the water that passes through the sulphur recovery and naphtha

recovery units. These recovery units clean up the water by removing sulphur (and coincidentally ammonia) and recycling naphtha. Essentially, wherever sulphur is produced or removed so is ammonia. The quality of these waste streams has improved and today much less ammonia is released into the tailings ponds via sour water than previously. Secondary ammonia sources include the knock out pot (a collector at the bottom of the flares) and spent amine which is used as a sulphur scrubber.

These contaminants (*i.e.*, naphthenic acid and ammonia) are of concern as they are toxic to aquatic organisms. A major source of acute toxicity to rainbow trout has been traced to naphthenic acids extracted from oil sands fine tailings (AEP, 1996; MacKinnon and Boerger, 1986). Ammonia is also acutely toxic to trout (USEPA, 1985). Comparing results from toxicity tests (Rainbow Trout 96 h LC50) conducted by Thurston et al. (1981) with those conducted for Dyke water samples it is apparent that approximately 50% of the toxicity observed is due to ammonia (Bishay and Nix, 1996). Therefore a treatment system that removes naphthenic acids and ammonia, and concomitantly the toxicity is required.

1.2 Wetlands as wastewater treatment facilities

Wetlands have been successfully used in treating domestic or municipal wastes (*e.g.*, in northern Quebec by Dubuc et al., 1986), urban runoff (*e.g.*, in Lake Tahoe Basin, Nevada by Reuter, 1992) and industrial wastes (*e.g.*, acid mine drainage in Colorado by Morea et al., 1990), etc. A variety of physical, chemical and biological processes within wetlands are responsible for removing "target contaminants" (Table 1.1). There are only a few examples (*e.g.*, Amoco, Litchfield and Schatz, 1989; Imperial Oil Ltd., Nix et al., 1993) of wetlands being used to treat wastewaters from petrochemical facilities or other sources of organic chemical wastes, and therefore Suncor has undertaken a study to assess the treatment effectiveness of constructed wetlands on oil sands wastewater (Hamilton et al., 1993).

A preliminary study of contaminated natural wetlands on the Suncor lease was conducted in October 1990 (Hamilton and Nix, 1991). Both contaminant removal and toxicity reduction were observed from "inflow" to "outflow". For example, total ammonia nitrogen was reduced 23% while total extractable hydrocarbons (TEH; which included naphthenic acids) were reduced 46%. The current study was undertaken based on these observations.

1.3 Objectives and Approach

There are five major issues surrounding the potential use of wetlands, at a northern latitude, to treat oil sands wastewater:

1. Do wetlands treat oil sands wastewater?
   - *i.e.*, are contaminant concentrations lower in the outflowing water than inflowing water

2. How well do wetlands treat this wastewater?
   - *i.e.*, at what rate are contaminants removed

3. Where do the contaminants go?
   - *i.e.*, are they degraded, or accumulated and where do these processes occur

4. What factors affect wetland treatment efficiency of oil sands wastewater and can these factors be optimized?
   - *i.e.*, are there minimum temperature requirements or maximum contaminant loads

5. Is treatment sustainable?
   - *i.e.*, are wetland functions such as macrophyte productivity/decomposition or nutrient cycling affected by the wastewater or treatment process such that effective treatment is not sustainable

To address these issues, nine constructed wetlands trenches were built in 1991 (Figure 1.3; Appendix A). Wastewater inputs began in 1992 and continued in 1993 and 1994. The flow rate of the wastewater varied year to year. Pond water was not tested in 1994. Instead, each of the three Pond water trenches were split in half lengthwise such that six flow rates of Dyke water could be tested. In addition to monitoring these constructed wetlands, the contaminated natural wetlands (Appendix A) were also monitored to observe the potential for long term impacts. Reference wetlands (*i.e.*, natural wetlands off the Suncor lease; Figure 1.1; Appendix A) were monitored for comparison between the treatment wetlands and uncontaminated natural wetlands.

Chapter 2 addresses 1) treatment efficiency by measuring ammonia inputs and outputs and estimating removal rates as the difference and by comparing these observed removal rates with those predicted by models developed in other studies, 2) contaminant (*i.e.*, ammonia) fate by measuring nitrogen storage pools (*i.e.*, sediment and macrophyte tissues) and physical and biological removal processes (*i.e.*, ammonia volatilization and nitrification/denitrification), 3) factors affecting treatment efficiency by monitoring removal (*i.e.*, treatment efficiency) at various loads and considering the impact of temperature, pH, dissolved oxygen, nutrients and hydrocarbons as they pertain to ammonia removal.

Chapter 3 addresses 1) hydrocarbon removal efficiency by measuring hydrocarbon inputs and outputs to estimate removal by the difference, and 2) potential contaminant fate pathways were discussed.

Chapter 4 addresses treatment sustainability by assessing the potential impacts of the treatment waters on macrophyte productivity and decomposition that represent wetland function.

Table 1.1 Physical, chemical and biological contaminant removal mechanisms in aquatic systems. (Stowell et al. (1980), reproduced by Watson et al. (1989)).

Mechanism		Effect[a]	Contaminant Affected	Description
Physical	Sedimentation	Primary	settleable solids	Gravity settling solids (and constituent contaminants) in pond/marsh settings.
		Secondary	colloidal solids	
		Incidental	BOD, nitrogen, phosphorus, heavy metals, refractory organics, bacteria, virus	
	Filtration	Secondary	settleable solids, colloidal solids	Particulates filtered mechanically as water passes through substrate, root masses, or fish.
	Adsorption	Secondary	colloidal solids	Interparticle attractive force (Van der Waals force).
Chemical	Precipitation	Primary	phosphorus, heavy metals	Formation of or coprecipitation with insoluble compounds.
	Adsorption	Primary	phosphorus, heavy metals	Adsorption on substrate and plant surface.
		Secondary	refractory organics	
	Decomposition	Primary	refractory organics	Decomposition or alteration of less stable compounds by phenomena such as UV irradiation, oxidation and reduction.

	Mechanism	Effect[a]	Contaminant Affected	Description
Biological	Microbial Metabolism[b]	Primary	colloidal solids, BOD, nitrogen, refractory organics, heavy metals	Removal of colloidal solids and soluble organics by suspended, benthic and plant-supported bacteria. Bacterial nitrification/denitrification. Microbially mediated oxidation of metals.
	Plant Metabolism[b]	Secondary	refractory organics, bacteria, virus	Uptake and metabolism of organics by plants. Root excretions may be toxic to organisms of enteric origin.
	Plant Absorption	Secondary	nitrogen, phosphorus, heavy metals, refractory organics	Under proper conditions, significant quantities of these contaminants will be taken up by plants.
	Natural Dieoff	Primary	bacteria, virus	Natural decay of organisms in an unfavourable environment.

a P = primary effect; S = secondary effect; I = incidental effect (effect occurring incidental to removal of another contaminant)

b metabolism includes both biosynthesis and catabolic reactions

Figure 1.1 Study sites around the Suncor mine site.

Figure 1.2 Aerial photograph of Suncor Lease 86.

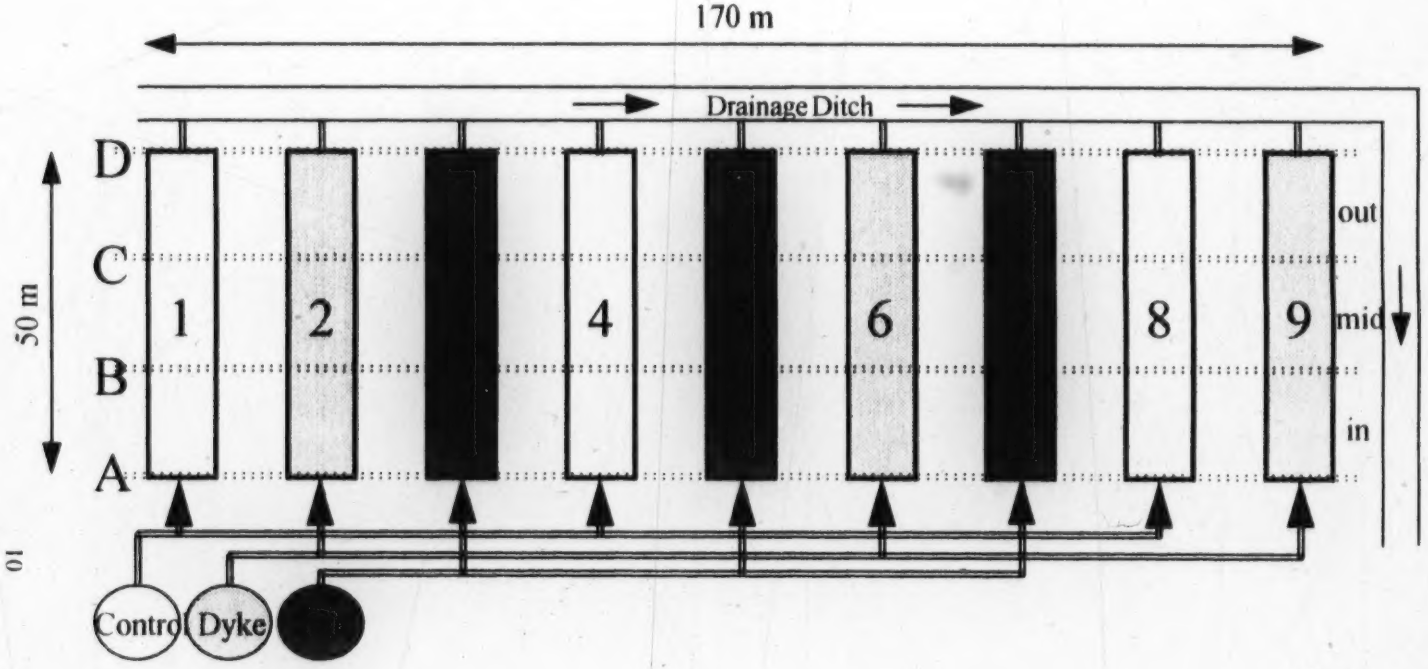

Figure 1.3 Schematic of the Suncor Constructed Wetlands research facility.

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2.0 AMMONIA REMOVAL IN CONSTRUCTED WETLANDS RECEIVING OIL SANDS WASTEWATER

2.1 Introduction

Significant sources of energy are currently obtained from mining of oil-rich sands in northern Alberta (currently more than 15 % of Canada's annual oil needs). Active mining leases during this study were about 26,600 ha, which produced about 300,000 barrels of oil per day (bpd). Recent approvals for new mines include development of another 18,400 ha. Should the currently proposed mines become active a total of about 54,000 ha would be disturbed. These surface mining processes disturb large areas of the landscape which will require reclamation. Additionally, the extraction process produces large volumes of waste tailings that contain various constituents of environmental concern. This study provides a pilot experiment using constructed wetlands to mitigate the environmental impacts of oil sands mining.

Suncor Inc., Oil Sands Group (Suncor) is mining oil sands in northeastern Alberta, Canada, 25 km north of Fort McMurray. The mining and subsequent conversion of oil sands bitumen to synthetic crude oil began in 1967. The Clark Hot Water Extraction Process used to extract bitumen from the oil sands produces a waste tailings. These tailings, made up of sand, clay, water and unrecovered bitumen, are stored in large tailings ponds. One component of tailings, the fine clays known as fine tailings, settle (*i.e.*, release water) very slowly. Therefore, there is potential for the release of contaminated water as leachate and/or surface run-off to terrestrial and/or aquatic systems as these tailings ponds are reclaimed.

A treatment system is required to mitigate the environmental impact of leachate and/or run-off water. Both organic (*e.g.*, hydrocarbons) and inorganic (*e.g.*, ammonia) contaminants are of concern. A constructed wetlands treatment system, which was considered possible because of its potential for long-term sustainability and low cost was studied. In this study, leachate from saturated tailings pond sand dykes (hereafter referred to as Dyke water) and tailings pond top water (hereafter referred to as Pond water) were treated in a pilot field-scale constructed wetlands facility.

A variety of physical, chemical and biological processes within wetlands are responsible for removing contaminants. However, there are few examples of wetlands being used specifically to treat wastewaters from petrochemical facilities or other sources of organic chemical wastes (Hamilton et al., 1993). The primary contaminants in the wastewaters studied were naphthenic acids and ammonia. However, the focus of this chapter was ammonia removal.

Ammonia is of concern because of its role in eutrophication, increased oxygen demand in the receiving environment and its toxicity to many aquatic organisms. Excessive nitrogen loading may lead to eutrophication of the receiving environment, especially if phosphorous loading is already elevated (Wetzel, 1983). As ammonia is oxidized via nitrification approximately 4.6 g of oxygen is consumed per gram of ammonium nitrogen oxidized, which can deplete oxygen in the aquatic environment (Reddy and Patrick, 1984). Ammonia is toxic to a variety of aquatic organisms. Unionized ammonia (NH_3) is the toxic fraction of total ammonia (NH_3 and NH_4^+). The fraction of unionized ammonia varies with pH and temperature as does its toxicity. Canadian (CCME, 1987) and US (USEPA, 1985) water quality guidelines/criteria reflect this. Total ammonia concentration should not exceed 0.93 mg L^{-1} at a pH of 8 and temperature of 20°C for the protection of aquatic life (CCME, 1987). Ammonia occurs in oil sands wastewater at consistently higher concentrations (*i.e.*, 10 - 15 mg L^{-1}) than recommended by the water quality guidelines and therefore a treatment system is required.

A variety of physical, chemical and biological processes in wetlands act to translocate and transform nitrogen. In wetlands receiving an elevated nitrogen load these processes may act together to effectively remove nitrogen from the water column (Watson et al. 1989). Physical, chemical and biological translocation processes include: particulate settling, diffusion of dissolved forms, sorption of soluble forms on substrate, ammonia volatilization and plant uptake. These processes also have opposite/countervailing processes which return nitrogen into the water column (*e.g.*, resuspension, litter fall, diffusion). Transformation processes may also remove nitrogen (*e.g.*, nitrification/denitrification, assimilation) and others may return nitrogen (*e.g.*, ammonification/mineralization, nitrogen fixation) to the water column.

It is important to understand the translocation and transformation processes acting to remove nitrogen when designing treatment wetland

systems (Kadlec and Knight, 1996). That is, are the contaminants simply retained in the wetlands (*e.g.*, sequestered in sediments or plants) and potentially available to return to the water column, thereby reducing wetland treatment efficiency. Alternatively, are the contaminants permanently removed from the system via volatilization and nitrification/denitrification. The primary nutrient removal mechanisms are microbial transformation and sedimentation translocation processes. Denitrification is believed to be the primary removal mechanism in wetlands, especially those receiving nitrogen rich wastewater (Hammer and Knight, 1994). Under specific conditions plant uptake may be a significant removal mechanism (*e.g.*, Rogers et al., 1991), while ammonia removal via volatilization may also be significant at pH 8.5 and above (Reddy and Patrick, 1984).

Ammonia can follow several pathways in wetlands: 1) uptake by biota, 2) immobilization by ion exchange, 3) nitrification by bacteria. Plants can take up ammonia through their root systems, as can anaerobic microbes (Mitsch and Gosselink, 1993). Both convert ammonia to organic matter. Ammonia can be immobilized in the sediments via ion exchange onto negatively charged particles (Mitsch and Gosselink, 1993). Nitrification, the microbial conversion of ammonia to nitrate, is the first step in the removal of the ammonia from wetlands. Nitrification occurs in a thin oxidized layer at the surface of the sediments (Mitsch and Gosselink, 1993) and in the oxidized plant rhizosphere (Reddy and Graetz, 1988). Denitrification, the microbial conversion of nitrate to dinitrogen (N_2) (and in lesser amounts nitrous oxide, N_2O) under anaerobic conditions, completes the process of ammonia removal.

Although ammonia removal was expected to occur in constructed wetlands receiving oil sands wastewater, contaminant fate and treatment efficiency were unknown. Because nitrification/denitrification are microbial processes which occur optimally at higher temperatures than usually observed in northern Alberta (57° N), actual removal rates may be slower than observed elsewhere. Nitrification may be inhibited by contaminants such as phenol (Bitton, 1994; Richardson, 1985) which are present in oil sands wastewater. Nitrification may also be inhibited by naphthenic acids above threshold concentrations (Sobolewski and MacKinnon, 1996). In addition, nitrifiers compete with heterotrophic bacteria for various resources such as oxygen (Barnes and Bliss, 1983); and therefore, nitrification may be limited due to competition from bacteria mineralizing the hydrocarbon contaminants. Thus,

in this study, nitrification (hence ammonia removal) may be impacted by the northern latitude, hydrocarbon contaminants and competition with heterotrophic bacteria.

The objectives of this study were to determine:

- ammonia removal rates under different wastewater loading rates;
- fate of the ammonia removed; and
- treatment efficiency of ammonia removal compared with literature values.

2.2 Methods

The general approach involved monitoring nine constructed wetland trenches over a three year period. Ammonia removal was estimated by measuring the difference in input and output ammonia concentration and water flow. Contaminant fate was assessed by measuring ammonia input/output loads, changes in storage (*e.g.*, seqùestering in sediments or plant uptake) and removal processes (*e.g.*, denitrification and ammonia volatilization). The relative treatment efficiency was assessed by comparing observed removal with predicted removal using three models.

2.2.1 Site Description and Experimental Design

Experimental Facility

The Suncor experimental constructed wetlands are located in northeastern Alberta, Canada, 25 km north of Fort McMurray (57°04'N 111°28'W). They are located southwest of Tailings Pond 2 between the tailings pond and Highway 63 (Figure 1.1). They were constructed in May and June 1991 and cover an area of approximately 1.4 ha (Figure 1.3). Nine trenches were constructed in 1991 with the following characteristics:

- cell dimensions - 50 m by 10 m at the top and 2 m at the bottom
- side slope - 2:1
- trench slope - 0.5 % (equivalent to a drop of 0.25 m over 50 m)
- mean depth - 0.35 m
- area - 175 m^2

- water volume - 52.5 m^3 (based on 50 m x 3.5 m x 0.35 m x 0.9 porosity)
- liner - 40 mil high density polyethylene
- substrate - 0.45 m of sand topped with 0.15 m of organic muskeg soil
- vegetation - 300 *Typha latifolia* (cattail) shoots and 60 *Scirpus validus* (bulrush) culms (bearing 6 - 15 shoots) were planted in each trench in June 1991
- establishment - 1 year

Experimental Design

Treatment waters were applied to the nine trenches in a randomized block design. Three replicate Control trenches were compared with treatment trenches (Dyke or Pond). The experimental design changed (*i.e.*, flow rates) from year to year (Table 2.1).

Monitoring Programme

There were two sampling schemes depending on the type of analysis: 1) four sampling stations from inflows to outflows (*i.e.*, A, B, C, D) were followed for water quality and water chemistry, and 2) three stations from inflows to outflow (*i.e.*, in, mid, out) were followed for sediment and aquatic emergent macrophyte (hereafter referred to as macrophyte) tissue chemistry. In the four station sampling scheme, Station A samples were taken from the inflow pipes, Station B was located 15 - 17 metres downstream of the inflow to each trench, Station C 30 - 34 metres downstream of the inflow, and Station D samples were taken from the outflow pipe/weir (50 m downstream of the inflow). In the three station sampling scheme, "in" samples were collected from within the first third (0 - 15 m) of each trench, the "mid" from the second third (16 - 30 m) and the "out" from the last third (31 - 45 m).

Sample frequency was limited in 1992 due to water limitations (*i.e.*, water was trucked in 1992 rather than pumped as in 1993 and 1994). In 1993 and 1994, water samples were collected as frequently as weekly to ensure that the sample frequency was at least as often as trench turnover (*i.e.*, within the estimated mean hydraulic retention time of 7 to 18 days).

Sediment and tissue sample frequency was one to three times per study year. In 1994, *in situ* measurements for ammonia volatilization and denitrification were made two and three times, respectively.

2.2.2 Sample Collection

Water and Sediment

Water samples were collected and shipped in coolers with ice packs to the laboratory the same day to ensure sample analysis was initiated within 24 h. Sediment samples were collected using a plastic corer (5 cm in diameter) with only the top 1 cm being collected. Several grab samples were collected at each station and placed in "whirl pack bags" to ensure a minimum of 50 g of sample. Samples were collected and shipped in coolers with ice packs to the laboratory.

Plants

Tissue samples were collected from *Typha latifolia* (cattail) and *Scirpus validus* (bulrush) shoots and roots. A total of three whole plants (i.e., shoot and root) for each species were collected from each trench (*i.e.*, one sample each from each sampling location along the trench). Shoots and roots were separated, and therefore a total of 12 samples (*i.e.*, three zones sampled for root and shoot for each species) per trench were collected. Samples were dried at ~ 40°C and ground using a coffee grinder after collection before analysis.

2.2.3 Sample Analysis

2.2.3.1 Water Chemistry

Three laboratories, the Limnology Laboratory at the University of Alberta, Edmonton, AB; Suncor Laboratory, Fort McMurray, AB and ASL (Analytical Services Laboratory), Vancouver, BC conducted the analyses. Most of the analyses were conducted by the University of Alberta; however, initially the other two labs were used. The relative percent difference (RPD) for ammonia within the three labs was 11 %, 3 % and 11 % for the University of Alberta, Suncor and ASL (Appendix B). The RPD was 21 % between ASL and Suncor and University of Alberta and Suncor (Appendix B). University of Alberta methods are detailed below, while the other labs used

APHA (1989) protocols for the various water chemistry parameters which are detailed in Appendix B.

Ammonia was determined from an unfiltered sample using the phenolhypochlorite method of Solórzano (1969) with the prepared samples being analyzed on the Technicon AutoAnalyzer. Nitrite-nitrate was determined from a filtered sample (0.45 µm HAWP Millipore filter) using the cadmium-copper reduction method of Stainton et al. (1977). TKN was determined using the sulphuric acid-copper sulphate method of D'Elia et al. (1977) and digested samples were analyzed using the Technicon AutoAnalyzer.

2.2.3.2 Sediment and Tissue Chemistry

Exchangeable ammonia and exchangeable nitrite-nitrate nitrogen in sediments were determined using the method of Bremner (1965). Total nitrogen (TN) in sediment and tissue samples were analyzed using a Control Equipment Corporation Elemental Analyzer (240 - XA) following the particulate carbon and nitrogen method of Stainton et al. (1977).

2.2.4 *In situ* Denitrification

Although there is no one universally satisfactory method for measuring denitrification (Arah et al., 1991), the acetylene inhibition technique was used in this study (in addition to the N mass balance approach) as it is a relatively easy and rapid technique and has been one of the most frequently used methods (Seitzinger et al., 1993). In this study, denitrification was measured *in situ* modifying methods used in Struwe and Kjøller (1990) and Chan and Knowles (1979).

Field incubations were made in 20 L plastic buckets placed upside down over the sediment surface. The buckets had two sample ports: on top (*i.e.*, in the bottom of the bucket) and below the air-water interface (*i.e.*, on the side of the bucket). Acetylene was supplied at a rate of 340 mL/min for 6 min through 6.35 mm (1/4") teflon hose and dispersed through the water column via a plastic aerator inserted through the top sample port. This was the equivalent to supplying approximately 2 L acetylene to reach the inhibiting (N_2O to N_2) concentration of 10 % by volume (Chan and Knowles, 1979). Chan and Knowles (1979) found that mixing for 5 min was sufficient to disperse the acetylene evenly, so during acetylene flow the hose was

turned by hand near the sediment-water interface to enhance mixing. The sample ports were 12.7 mm (1/2") holes plugged with Vaccutainer tube rubber stoppers. The top stoppers were removed during bucket placement and acetylene addition. Once acetylene addition was completed the hose was removed and the port stoppered.

Air samples were withdrawn following a 24 h incubation period using a 30 mL disposable syringe and needle through the stopper. Samples were then expelled into 22 mL glass vaccutainer tubes with positive pressure (*i.e.*, 30 mL air samples). Prior to use in the field, vaccutainer tubes were opened and resealed following the addition of silica gel and reevacuated (*i.e.*, returned to vacuum). Water samples were removed similarly, except a 60 mL syringe was used. After 30 mL of water was drawn into the syringe, 30 mL of helium was also drawn into the syringe. The syringe was sealed by stoppering the needle. Samples were then shaken for 1 minute (to equilibrate the gases; McAuliffe, 1971) and the gas sample expelled into 22 mL glass vaccuatiner tubes with positive pressure. Vaccutainer tubes were then resealed with silicone and transported to the University of Alberta for analysis by Gas Chromatography within two month of collection. Helium blanks were analyzed to estimate background nitrous oxide in the gas equilibrated samples (*i.e.*, water samples).

The acetylene inhibition technique inhibits dinitrogen (N_2) formation and therefore prevents the final conversion of nitrate nitrogen to dinitrogen (*i.e.*, denitrification). The reaction is stopped at nitrous oxide (N_2O) which can be directly measured using gas chromatography techniques. The N_2O in gas samples was measured using gas chromatography with a ^{63}Ni electron capacity detector (ECD). In addition, carbon dioxide and methane were also measured using gas chromatography with FID. Peak areas were determined. Areas were calibrated with known gas concentrations to estimate sample concentrations based on peak areas.

2.2.5 Ammonia Volatilization

Ammonia volatilization was predicted using ammonium nitrogen concentration and apparent ammonia volatilization rate constant (Freney et al., 1985) for pH 8, 20°C and 5 m/s wind velocity conditions (Kadlec and Knight, 1996). Therefore volatilization may have been overestimated because pH was at or below pH 8, except in 1992, mean temperatures were less than 20°C and wind speed estimated from monthly wind runs was < 1m/s. In addition in

1994, direct measurements were attempted using phosphoric acid traps. Overturned 10 L plastic buckets were used to isolate a portion of the water surface. A 60 mL beaker was filled with 30 mL of 2 % phosphoric acid (Denmead et al., 1976) as a trap for ammonia and placed on a styrofoam float (1.5 x 10 x 15 cm) under the overturned bucket. The bucket lip was submerged 2 - 4 cm below the water surface to maintain a seal. Traps were left for several days to accumulate ammonia in the phosphoric acid traps. The acid and collected ammonia were analyzed for ammonia as per water sample analysis.

2.2.6 Nitrogen Budget

Nitrogen input and output loads were estimated from input and output nitrogen concentrations and input and output water flows (Appendix C). The difference between input and output load was assumed to be the load removed or retained. The load retained (*i.e.*, change in storage) was estimated by measuring nitrogen in several compartments (*e.g.*, sediments) during 1993 and 1994. The observed nitrogen in the sediments and plants in the Dyke and Pond trenches was corrected by subtracting the total in the Control trenches to account for background nitrogen and calculate nitrogen storage. The load removed was estimated by measuring the nitrogen elimination processes of volatilization and denitrification in 1994. Denitrification in the constructed wetlands trenches was measured and used to estimate loss of nitrite-nitrate nitrogen (*i.e.*, loss of nitrogen to the atmosphere) after nitrification of ammonia. Ammonia volatilization from the constructed wetlands was measured and used to estimate loss of ammonia to the atmosphere.

Mass balance equations were determined by estimating the various storage compartments together with loss processes. The following mass balance equation was used to estimate the removal efficiency of the wetlands under various loading rates:

$$inflow = outflow + nitrification/denitrification + volatilization \pm change\ in\ storage$$

In years where either compartments or processes were not measured, this equation was rewritten to estimate the unknown compartment/process.

2.2.7 Statistical Analysis

2.2.7.1 Water Chemistry

The water chemistry data were not statistically analyzed because of a lack of variation (as many control samples and some outflow samples had values less than the detection limit). Data were graphically interpreted to assess whether there was a difference between treatment waters or from inflow to outflow for a given wastewater. It was generally obvious when some treatment had or had not occurred and when the treatment observed had or had not approached conditions observed in the Control trenches.

2.2.7.2 Sediment and Tissue Chemistry

Sediment and tissue concentration (mg kg^{-1}) data were tested for significant difference between treatment waters. All statistical analyses were performed using the SYSTAT statistical package (Wilkinson, 1990). Following convention, a probability of $\alpha \leq 0.05$ was used to define statistical significance.

Repeated measures analysis of variance (ANOVA) tests were conducted on the total nitrogen and exchangeable ammonia in sediments and the total nitrogen and phosphorous in tissues to assess the effects of wastewater type. Individual trenches were used as replicates of the treatment water type (*i.e.*, the treatments were sampled in triplicate). Measurements were replicated three times in each sampling period (*i.e.*, date) or zone (*i.e.*, in, mid, out) for most sediment data, while tissue data were only replicated spatially not temporally in each study year. Repeated measures design is the same as a split plot design, with the treatments applied to the whole plots or trenches and the sampling period and zone applied within plots or trenches. No trench effects were assumed. Post-hoc contrasts were used to determine which means were significantly different using Bonferroni adjusted alpha levels (*i.e.*, critical level of 0.05 divided by the number of contrasts tested). Testing a subset of comparisons rather than all possible pairwise comparisons (*e.g.*, Tukey HSD) often gives more power to the analysis (Day and Quinn, 1989; Wilkinson, 1990). Repeated measures ANOVAs were conducted for each parameter (*e.g.*, total nitrogen in bulrush root, exchangeable ammonia in sediments, *etc.*) and year separately (*i.e.*, 1993 and 1994).

2.2.7.3 Volatilization and Denitrification

A T-test between the Control and Dyke Drainage treatments using the trench means of data over the two sampling periods and three zones was done instead of repeated measures ANOVA. Trench means were used for statistical analysis due to the high number of missing data (*e.g.*, volatilization samples lost due to muskrats; all stations within each trench were not measured for denitrification due to the length of time required to set-up and take samples for each station) making other types of statistical analysis difficult.

2.3 Results and Discussion

2.3.1 Water Chemistry

Ammonia-ammonium Nitrogen

In all study years ammonia concentrations were reduced from inflow to outflow of the treatment wetlands (Table 2.2). Control inflow concentrations were at least an order of magnitude lower than in Dyke and Pond inflows. Dyke inflow concentrations were in the range of 10 to 15 mg L^{-1}, and Pond inflow concentrations were in the range of 10 to 12 mg L^{-1}. Control inflow concentrations were generally < 0.05 mg L^{-1}; except in 1992 when Ditch water (0.2 mg L^{-1}) rather than Loon Lake water was used. On average the inflow concentrations of Dyke and Pond water were lower in 1992 compared with 1993 and 1994. Average Dyke outflow concentrations were in the range of 0.15 to 12 mg L^{-1}, and Pond outflow concentrations were in the range of 0.25 to 10 mg L^{-1}. Control outflow concentrations were generally < 0.1 mg L^{-1}. On average the outflow concentrations in Dyke and Pond water were lower in 1992 than 1993; while Dyke outflow concentrations in 1994 were intermediate.

Although ammonia removal was substantial (ranging from 32 - 99 %), an order of magnitude difference between the Control trench outflows and either the Dyke or Pond trench outflows remained. In 1992 and 1994, removal rates were in the range of 44 % to 99 %; however, in 1993 removal rates were much lower (20 - 40 %) presumably because of the increased ammonia loading.

In 1993 ammonia concentration in the inflow was slightly higher in Dyke and Pond wetlands than in 1992, while ammonia concentration in the outflow was much higher reflecting the substantially higher loading in 1993. Coincident with the higher inflow ammonia concentration (which was not planned) in 1993, the design flow was increased to 6 L/min (from 2 L/min). However, the total load removed was the same or slightly higher in 1993 than 1992, suggesting that the removal capacity of the constructed wetlands trenches had been met. In 1994, ammonia removal efficiency was intermediate compared with efficiency in 1992 and 1993.

Nitrogen removal efficiency typically ranges between 50 % to 97 % (Watson et al., 1989) in similar wetlands systems. Removal efficiency (as percent of input loads) in the current study was comparable, and ranged from 32 % to 99 % (Table 2.3). Removal efficiency was related to ammonia loading rate and possibly by the contaminant (*e.g.*, hydrocarbons) loading. Thus, removal efficiency tended to be greater at lower loading rates, and more efficient in the less toxic Dyke water (Figure 2.1). At loading rates of 190 mg m^{-2} d^{-1} removal efficiency averaged > 90 %, while for higher loading of 270 mg m^{-2} d^{-1} removal efficiency averaged 75 %. Even lower removal efficiency (32 to 42 %) was observed for higher loading rates (605 to 785 mg m^{-2} d^{-1}), although similar loads were removed.

Ammonia removal efficiency tended to decrease with higher ammonia loading rates; however, it is likely other factors also affected ammonia removal. These factors include: temperature, dissolved oxygen (DO), pH, hydraulic retention time, hydrocarbon load. All of these factors (except temperature) tended to follow a trend with ammonia loading (*e.g.*, higher ammonia loading the higher the hydrocarbon loading, higher ammonia loading the lower the DO).

Nitrite-nitrate Nitrogen

In general, nitrite-nitrate nitrogen (NO_x or nitrate) concentrations were similar or reduced from inflow to outflow of the treatment wetlands; that is, they were reduced in 1992 and stayed about the same in 1993 and 1994. In 1992 inflow concentrations were elevated, especially in Dyke water (*e.g.*, 6 mg L^{-1}). The cause of the elevated concentrations is unknown, and could be due to either the delivery method which may have substantially aerated the Dyke water or the inherent variability in the water from year to year (*e.g.*, the phreatic water level in the dyke moves up and down and may

have been impacted by a highly fertilized zone on the tailings pond dyke). In 1993 and 1994, nitrate was low (*i.e.*, < 1 mg L^{-1}) in both Control and Dyke inflow waters.

Nitrate tended to decrease from inflow to outflow in the Control trenches and increase in the Dyke trenches. The decrease in the Control trenches can be attributed to either organism uptake and/or denitrification (*i.e.*, bacterial conversion to atmospherical N_2 or N_2O). The increase in the Dyke trenches can be attributed to nitrification (*i.e.*, bacterial conversion of ammonia to nitrate nitrogen).

Nitrate was similar between the Dyke and Pond inflows and outflows in 1993 and 1994, although nitrate always increased downstream of Station A but did not remain elevated. The station with the highest concentration of nitrate shifted from B to D over the study season especially in 1994 (Figure 2.2). This shift may indicate a "saturation point" (*i.e.*, overloading by ammonia and/or other contaminants, or oxygen limitation for nitrification). The shift in the maximum concentration of nitrate corresponds to the shift in the zone of maximum ammonia removal suggesting saturation. Early in the 1994 study season almost all of the ammonia was removed between Stations A and B, while late in the season little was removed between A and B and the rest was evenly removed between B and C and C and D (Figure 2.3). Although these same trends were not as obvious in 1993, perhaps due to the overloading of the wetland trenches, the proportion of the total ammonia removal generally decreased between Stations A and B.

Total Kjeldahl Nitrogen

Total kjeldahl nitrogen (TKN) is a measure of organic nitrogen plus ammonia-ammonium nitrogen. The ratio of TKN to ammonia nitrogen in the water of both Dyke and Pond trenches was close to 1 which suggests that very little of the TKN was organic. There was no change or a slight decrease in this ratio from inflow to outflow suggesting that no more organic nitrogen was leaving the wetlands than was entering. TKN in the Dyke and Pond outflows was higher than in the Control outflows reflecting the differences in ammonia nitrogen (Table 2.2). In the Control wetlands, ammonia was only a small percentage of TKN (< 5 %).

2.3.2 Sediment Chemistry

Exchangeable Ammonia

Exchangeable ammonia concentrations were lower in the sediments of the Control trenches than either the Dyke or Pond trenches (Table 2.4; Figure 2.4). These differences were significantly different in both 1993 (F = 85.7, p < 0.001) and 1994 (F = 25.0, p = 0.008). In addition, trends over time and distance from the inflow were observed.

Trends of increasing ammonia with continued ammonia loading were significant in 1994 (F = 4.9, p = 0.042) for Dyke trenches (Figure 2.4). In the Dyke trenches, exchangeable ammonia increased in 1993 from 14.8 mg kg^{-1} in June to 34.4 mg kg^{-1} in September, and in 1994 it increased from 9.6 mg kg^{-1} in June to 13.6 mg kg^{-1} in August to 20.1 mg kg^{-1} in September. Ammonia accumulated over time in the sediments, but when wastewater (ammonia) application was discontinued in the autumn and winter, ammonia concentrations in the Dyke trench sediments decreased. For example between 1993 and 1994, the autumn 1993 sediment ammonia concentration of 34.4 mg kg^{-1} decreased over winter to 9.6 mg kg^{-1} by June 1994.

Trends of decreasing ammonia from inflow to outflow were significant in 1993 (F = 63.7, p < 0.001) and 1994 (F = 12.3, p = 0.004) for Dyke trenches (Figure 2.5). In the Dyke trenches, exchangeable ammonia decreased in 1993 from a mean of 30.8 mg kg^{-1} at the inflow to 18.6 mg kg^{-1} at the outflow, and in 1994 it decreased from 22.9 mg kg^{-1} at the inflow to 8.1 mg kg^{-1} at the outflow. The decrease in ammonia in the sediments downstream of the inflow reflected changes in water chemistry (*i.e.*, ammonia is removed from the water column at upstream locations; therefore, there is less to enter the downstream sediments). In addition, the higher concentrations observed in 1993 were likely due to the higher ammonia loading.

Exchangeable Nitrate

Sediment nitrate was very low compared with ammonia (Table 2.4). This was expected since 1) nitrate inputs were low (*i.e.*, often less than detection limits), and 2) nitrate formation from ammonia is the rate limiting step in ammonia removal. Nitrification, the microbial process converting ammonia to nitrate, must occur prior to denitrification. Denitrification, the microbial process converting nitrate to dinitrogen which is released to the

atmosphere, is usually limited by nitrification (Mitsch and Gosselink, 1993). Therefore, low levels of nitrate were expected in the sediments, because as nitrates were formed they would diffuse to the anaerobic zones where they would be converted to dinitrogen. Nitrate was higher in the Dyke trenches compared with the Control trenches (Table 2.4); however, statistical analysis was not conducted due to the large number of values which were less than the detection limit (DL). Nitrate was less than the DL in all trenches in June and was generally higher in August than September.

Total Nitrogen

TN in the sediments was not significantly different among treatments (Table 2.4). No trends over time or distance downstream of the inflow were observed. The ammonia observed in the Dyke trenches was only about 0.01 to 0.02 % of the TN, which was not a significant proportion of the N in the sediment storage pool. In fact, the proportion ammonia was indistinguishable when TN in the Dyke trenches was compared with Control trenches making it difficult to quantify the nitrogen load retained in the sediments (as measured by TN).

In 1994, the ratio of total carbon to total nitrogen was 26.6:1 and 28.6:1 for the Control and Dyke trenches, respectively, while the ratio of total nitrogen (N) to phosphorous (P) was 6.6:1 and 5.5:1 for both Control and Dyke trenches, respectively. This suggests that significant total N accumulation in the sediments may not have occurred.

2.3.3 Macrophyte Tissue Chemistry

TN concentration in the macrophyte tissues collected from the Dyke and Pond trenches tended to be elevated compared with the Control trenches (Table 2.5; Figure 2.6). In 1993, TN was significantly different among the three treatments for both cattail (*Typha latifolia*) shoot (F = 10.4, p = 0.011) and root (*i.e.*, rhizome and root tissues; F = 10.9, p = 0.01) tissues. However, TN concentration was only different in bulrush (*Scirpus validus*) root tissues (F = 29.7, p = 0.001) and not bulrush shoot tissues. When differences were significant TN concentrations in tissues from Control trenches were lower than in tissues from the Dyke and Pond trenches. Although TN concentrations were generally higher in Dyke trenches than Control trenches in 1994, TN was only significantly different in cattail root tissues (cattail roots p = 0.001; bulrush roots p = 0.2).

Root TN concentrations tended to be higher in trenches receiving the higher ammonia loading (*i.e.*, Dyke and Pond trenches), more so than shoot concentrations. Ratios of N:P in tissues further supported these trends. Shoot N:P ratios for cattails (Control 10:1, Dyke 8:1) and bulrush (Control 9.4:1, Dyke 10.5:1) were similar between treatment waters as would be expected since there was no statistical difference between N tissue concentrations. However, root N:P ratios for cattails (Control 4.4:1, Dyke 7.5:1) and bulrush (Control 5.4:1, Dyke 7.5:1) were higher in the tissues from the Dyke trenches suggesting uptake of N. N was taken up by the roots in trenches with higher concentrations of ammonia in the water and sediments (*i.e.*, Dyke and Pond trenches). However, when the concentration data were corrected for biomass in each sampling zone these differences were no longer significant in 1993 (Figure 2.6) In 1994, these differences may have been significant (Figure 2.6); however, the data were confounded by muskrat "eat out" in the Control trenches.

2.3.4 Denitrification

Potential denitrification (*i.e.*, the conversion of nitrate to nitrous oxide/dinitrogen) was measured *in situ* using the acetylene blockage technique in 1994. Potential denitrification (*i.e.*, mg N_2O-N evolved per m^2 per day) was higher in the Dyke trenches than the Control trenches (Figure 2.7). Means for the Control and Dyke trenches over the four sampling periods and three zones were 0.04 mg N/m^2/day and 8.16 mg N/m^2/day, respectively. These means were significantly different (T = -8.042; p = 0.015). However, the measured denitrification rate of 0.19 kg N/wetlands/season accounted for only 4 % of the 4.8 kg ammonia N/wetlands/season removed in the Dyke trenches. This observation may be due to the limitations of the technique rather than the lack of occurrence of denitrification (Seitzinger et al., 1993; Dalsgaard and Bak, 1992).

The acetylene inhibition technique may underestimate denitrification rates. The acetylene inhibition technique fails to capture coupled nitrification/denitrification due to the inhibition of nitrification by acetylene (Seitzinger et al., 1993). No additional nitrate was added during the incubation period, only the nitrate present was available for denitrification. Consequently, denitrification as measured could have been underestimated. Standing stock of nitrate in the sediment and water were estimated as 1.23 mg/m^2 and 42.9 mg/m^2 based on mean nitrate nitrogen

concentrations of 0.1 mg kg^{-1} and 143 µg/L, respectively. Assuming the estimated standing stock of nitrate was present within the chamber during the incubation period, then the measured denitrification should have been higher. Acetylene may not reduce N_2O in the presence of some organisms which would lead to an underestimation of *in situ* rates (Dalsgaard and Bak, 1992). Additionally, the concentration gradient of N_2O may change as N_2O increases inside the chamber. The theoretical constant gradient is linear; however, the expected gradient will decrease over time (Lemke, 1997). If linearity is assumed then a downward bias of 34% may occur (Anthony et al., 1995). Hutchinson and Mosier (1981) developed an adjustment for this underestimate; however, the assumption required for the calculation only holds for a subset of samples (Anthony et al., 1995). Therefore, linearity was assumed, which could also have led to an underestimate of denitrification.

Nitrate loss measured as denitrification in other studies ranged from 60 to 70 % in unvegetated microcosms in a treatment wetland (Cooke, 1994), 75 to 90 % in a flow-through *Phragmites*/gravel subsurface wetland (Stengel et al., 1987), to about 90 % in soil microcosms in a treatment wetland (Bartlett et al., 1979). These values are much higher than those measured in this study (about 4 %; see later). Assuming the still unaccounted for ammonia was indeed nitrified/denitrified, then the proportion (about 87 %) would be comparable with denitrification measured in other studies (*e.g.*, Stengel et al., 1987). However, this may not be valid given the cooler temperatures (*e.g.*, Brodrick et al., 1988).

The rates observed in both Control and Dyke trenches were lower than the range of 60 to 87 mg m^{-2} d^{-1} observed in eight riparian wetlands (Seitzinger 1994). Although the riparian wetlands studied were selected to include various degrees of anthropogenic N inputs, N loading was not quantified (Seitzinger, 1994) making comparison with this study difficult. An average denitrification rate for marshes about 100 km north of Edmonton were 47.1 mg N/m^2/day (Mewhort, pers. com.). These rates were lower than those obtained by Seitzinger (1994), which were obtained under a higher incubation temperature. These denitrification rates probably reflect systems receiving a lower N load than in the Dyke trenches.

Seitzinger et al. (1993) has determined that the acetylene inhibition technique underestimates rates by 50 % due to failure to prevent reduction of N_2O and another 35 % due to inhibition of nitrification. However, even

assuming this degree of underestimation, the denitrification rate was still only 17.4 mg m^{-2} d^{-1}, considerably lower than 200 mg m^{-2} d^{-1} of N removed from the water. Either another removal pathway was dominant or perhaps under higher N loadings/denitrification rates, the proportion underestimated increases. Alternatively, proportionately higher numbers of organisms that are not inhibited by acetylene were present (*e.g.*, Dalsgaard and Bak, 1992) than in Seitzinger et al.'s (1993) study.

2.3.5 Volatilization

Loss of ammonia via volatilization (as measured by ammonia trapped in 2 % phosphoric acid solution) was variable. Control trenches exhibited very little ammonia volatilization compared with Dyke trenches (Figure 2.8). Means for the Control and Dyke trenches over the two sampling periods and three zones were 0.025 ± 0.039 mg N/m^2/day and 0.185 ± 0.060 mg N/m^2/day, respectively. These means were significantly different (T = -4.01; p = 0.016). The measured loss of ammonia via volatilization was about 0.004 kg $trench^{-1}$ $season^{-1}$ in the Dyke trenches or < 1 % of the ammonia removed. Ammonia volatilization as measured, may be an underestimate. The buckets used to trap volatilizing gases from the water surface may also prevent wind action that could have accelerated the volatilization rates. Wind speed, pH, temperature and ammonia concentration are the governing factors affecting ammonia volatilization (Freney et al., 1990).

A volatilization model was used to predict the volatilization rates, because the measured ammonia volatilization rates could have been an underestimate. The predicted rates were compared with the measured rates to assess the potential for significant ammonia removal via volatilization. Predicted ammonia volatilization (from a model developed by Freney et al., 1985) was one to two orders of magnitude greater than measured volatilization. The model equations were combined to calculate an ammonia emission rate constant based on the ammonia concentration in the water as follows (Kadlec and Knight, 1996):

$$J_v = k_{av} C_{LA,0}$$

where:

J_v = ammonia emission rate, g N m^{-2} d^{-1}

k_{av} = apparent ammonia volatilization rate constant, m/d

$C_{LA,0}$ = unionized ammonia in liquid phase at the water surface, g/m^3

The apparent ammonia volatilization rate (k_{av}) constant of 2.39 m/y (or 0.0065 m/d) was used. This model assumes a pH of 8, temperature of 20°C and wind speed of 5 m/s. This rate constant would likely a overestimate ammonia emission rates because the mean water temperature and pH were lower at 17.7°C and 7.6, respectively. Although the wind speed was not actually measured, the average wind speed was calculated from monthly wind runs to range from 0.4 m/s to 0.8 m/s, which was lower than the wind speed used (5 m/s) to calculate the K_{av}. K_{av} values were only available for wind speeds of 5 m/s. Using the K_{av} of 0.0065 m/d and assuming 0.57 mg L^{-1} unionized ammonia (*i.e.*, 3.82 % of 15 mg L^{-1} total ammonia at pH 8 and 20°C is unionized; USEPA 1979), the ammonia emission rate from the Dyke trenches was calculated as 3.7 mg m^{-2} d^{-1}. Volatilization was not a significant pathway, because pH was not consistently above 8.5 (Reddy and Patrick, 1984). Diurnal sampling was conducted in early September of 1994 and pH increased in the late afternoon; however, on average it remained below 8.5.

Given this and that the assumptions are overestimates of average *in situ* conditions, it is possible that the actual rate is approximated better by *in situ* acid traps than by the above model. Although the calculated volatilization rate is significantly greater than the measured rate it still would only account for less than 3 % of the ammonia removed from the Dyke trenches. Neither the measured or predicted rates suggest that ammonia volatilization played a significant role in nitrogen removal from the treatment wetlands.

2.3.6 Nitrogen Mass Balance

The mass balance for ammonia nitrogen in the constructed wetlands treatment trenches was determined for each study year (Table 2.6). Ammonia nitrogen in inflow and outflow water, change in storage and microbial removal processes were measured, and a mass balance for ammonia

nitrogen in the Dyke and Pond trenches was determined. In 1994, the only year with a complete budget, the difference between inflow and outflow (*i.e.*, the amount of ammonia "removed" or "retained" by the wetlands) was 4.8 kg trench^{-1} season^{-1} (206 mg m^{-2} d^{-1}), while the sum of the measured removal processes and change in nitrogen storage was only 2.35 kg trench^{-1} season^{-1} (101 mg m^{-2} d^{-1}).

Assuming the source of all the ammonia measured in the sediments was from the wastewater and not ammonification, then a significant portion of the input load was sequestered in the sediments. There was so much organic N (as measured by TN) in the sediments in both the Control and Dyke trenches that ammonia retention could not be detected. In fact, TN was higher in the Control (1.2 kg m^{-2}) trenches than Dyke (0.9 kg m^{-2}) trenches. However, ammonia removal to the sediments was about 101 mg m^{-2} d^{-1} (37.4 % of input nitrogen) for a total of 13,384 mg m^{-2} (Figure 2.9). This accumulation may be an overestimate since the amount of ammonia present at the beginning of the study year was assumed to be no more than what was in the Control trenches at the end of the study year (cf. Section 2.3.8). Conversely, this is only about 1.4% of the TN, which is within the error of the TN analysis, and therefore the measurement of TN in sediments may not accurately reflect the ammonia nitrogen accumulation during the study. Additionally, TN analysis may further underestimate ammonia accumulation because incorporation into organic matter would also not have been detected. Removal of ammonia nitrogen to the sediments was at least 49 % (2.3 kg trench^{-1} season^{-1}; 101 mg m^{-2} d^{-1}) of the ammonia nitrogen retained (more if immobilization occurred), while plant uptake accounted for approximately 2 % (0.10 kg trench^{-1} season^{-1} or 4.5 mg m^{-2} d^{-1}).

Nitrogen removal by plant uptake is not considered to be a main removal processes. Although plant uptake may reach 500 mg m^{-2} d^{-1} annually (van Oostrom and Russell, 1994), the majority of nutrients are leached back into the water at the end of each growing season (Richardson and Nichols, 1985). Klopateck (1975, 1978 cited in Richardson and Nichols, 1985) found that 48 mg N/m^2/d was translocated from wetlands soils to plants over the year and that about 42 % of this nitrogen was leached back into the water column at the end of the growing season. Plant uptake in a treatment system in California only accounted for 12 - 16 % of the nitrogen removed (Gersberg, 1986).

Volatilization and denitrification accounted for approximately 0.1 % (0.004 kg trench^{-1} season^{-1} or 0.22 mg m^{-2} d^{-1}) and 4 % (0.19 kg trench^{-1} season^{-1} or 10.6 mg m^{-2} d^{-1}) of the ammonia retained, respectively. Volatilization of ammonia may account for losses up to 100 mg m^{-2} d^{-1} at pH 8 (based on an empirical equation developed for predicting ammonia volatilization from flooded rice fields by Freney et al., 1985); however, based on the environmental conditions observed the model predicted that only 3.7 mg m^{-2} d^{-1} of ammonia could have been volatilized. Although denitrification is often assumed to be the primary removal process (Nichols, 1983), in this study it may only represent at most 50 % of the observed removal. However, denitrification (as measured) could not be verified experimentally to be a predominant pathway possibly due to the limitations of the technique rather than the lack of occurrence of denitrification (Seitzinger et al., 1993; Dalsgaard and Bak, 1992).

Although the removal processes and storage compartments measured did not account for all the ammonia nitrogen retained by the wetlands, these processes and compartments were expected to be responsible for the losses observed because there was no other removal pathway. It is unlikely that removal to the vegetation was significantly underestimated. Removal to the sediments may have been underestimated because incorporation of ammonia into organic matter would not have been detected by TN measurements. Potential denitrification rates may also have been underestimated. Although volatilization measured *in situ* may also be an underestimate because of reduced wind action over the sample site, it was not assumed to be a significant removal pathway because predicted rates were also low.

In estuarine constructed wetlands the dominant removal pathways include both accumulation in organic matter in the sediments and denitrification. Under lower nutrient loading the ratio of removal to the sediments and via denitrification is about 1.4:1, while under higher nutrient loading both processes increase though denitrification more so, such that the ratio flips to about 1:3 (Craft, 1997). Therefore, sediment retention and nitrification/denitrification were assumed to be the dominant ammonia removal pathways here also.

2.3.7 Treatment Efficiency

The capability of constructed wetlands, receiving oil sands wastewater, to remove ammonia was assessed by comparing observed effluent ammonia

concentrations with predicted concentrations using three different models (Figure 2.10; Appendix D). Model 1 is based on nitrification rates in attached growth biological reactors (Reed et al., 1994). Models 2 and 3 are based on ammonia removal in various wetlands. Model 2 is based on natural wetlands and free surface and submerged bed constructed wetlands (WPCF, 1990) and Model 3 is based on 17 free surface wetlands (Hammer and Knight, 1994). Since none of these models reflect only free surface constructed wetlands in northern latitudes, all three were examined to better understand the relative treatment efficiency of the constructed wetland trenches receiving Dyke and Pond water.

In general, the observed effluent ammonia concentrations from the constructed wetland trenches were significantly different from the predicted concentrations in 12 of the 15 data sets (Figure 2.10). For 8 of the 12 data sets, the observed treatment significantly outperformed the predicted treatment, while predicted treatment outperformed the observed treatment in four data sets.

Model 1 assumes that constructed wetlands are attached growth biological reactors and that their performance can be estimated by first-order plug-flow kinetics and is based on data for available surface area, hydraulic retention times and water temperature (Reed et al., 1994). Observed ammonia removal in 1992 - 1994 overlapped with the ammonia removal range predicted by Model 1. Since Model 1 reflects nitrification rates the similarity between the observed and predicted data indicated that the primary ammonia removal mechanism was likely nitrification/denitrification. Significant differences between three of the five observed and modelled data sets were noted; however, the observed outflow ammonia values were lower than the model values for two of these data sets (Figure 2.10). Although these differences may not be biologically significant, they can be explained by experimental error, the effects of mineralization, short-term plant uptake or ammonia volatilization. The constructed wetland trenches removed at least as much ammonia as expected from Model 1 in three of the five data sets (*i.e.*, significantly higher or not significantly different). This suggests that the performance of the trenches was neither inhibited by the petroleum hydrocarbons nor the northern location.

Model 2 is based on a regression analysis of data from constructed and natural wetland treatment systems (WPCF, 1990) and is based on hydraulic loading rate. Observed ammonia removal in 1992 - 1994 overlapped with

the ammonia removal range predicted by Model 2. However, significant differences between the observed and modelled data were noted for all years and treatment waters. The observed outflow ammonia values were generally comparable with model values except in 1993 where observed values exceeded predicted values substantially. These differences were likely due to the source data used in the derivation of Model 2. Although the input ammonia concentrations and loads fit in the range of the treatment wetlands used to derive the model, the inclusion of data from submerged beds may have increased removal efficiencies beyond that possible by the free surface wetlands used at Suncor. The comparison of predicted data from Model 2 with the observed data suggests that ammonia removal at Suncor may be somewhat inhibited by the petroleum hydrocarbons or the northern location. Temperature was not included in this model and may have had an effect since many of the wetlands used to derive Model 2 were from the southern United States. However, Mahli and McGill (1982) observed that optimum nitrification rates change with climate, so in cooler climates a lower optimum temperature for nitrification occurs.

Model 3 is based on a regression analysis of data from 17 free surface constructed wetland treatment systems (Hammer and Knight, 1994) and is based on ammonia loading. Observed ammonia removal in 1992 - 1994 overlapped with the ammonia removal predicted by Model 3. However, significant differences between the observed and modelled data were noted for all years and treatment waters; however, the observed outflow ammonia values were always lower than the predicted values. Although these differences may not be biologically significant, they can be explained by experimental error, and differences between systems with respect to mineralization, short-term plant uptake or ammonia volatilization. The constructed wetlands removed as much ammonia as expected from Model 3 and suggests the performance of the trenches were neither inhibited by the petroleum hydrocarbons nor the northern location.

Comparisons of the treatment wetlands with the modelled data (in the three models) suggests that the treatment efficiency in the Suncor constructed wetlands was somewhat lower than systems receiving similar ammonia loading under the conditions for Models 1 and 2, but comparable and even better in some cases than for Model 3. Model 3 was most representative of the conditions in this study, and the observed data were comparable or better than results predicted by this model. Therefore, ammonia removal

(*i.e.*, primarily nitrification/denitrification processes) was not impacted by the northern latitude of the study site, petroleum hydrocarbon contamination, and/or competition for resources.

Although this was only a three year study, there is potential for long-term treatment. Ammonia removal was consistent among the three years study, with the highest load being removed in 1993, although this was not the year with the highest efficiency. Unlike phosphorous, wetlands are expected to retain the rate of nitrogen removal and are likely to improve with age (Craft, 1997).

2.3.8 Long-term Treatment

The dominant removal mechanisms in this study were assumed to be nitrification/denitrification and sediment retention. Nitrification/denitrification completely removes nitrogen from the wetland to the atmosphere and is sustainable in the long-term (Craft, 1997; Johnston, 1991). Sediment retention occurs via sorption, and sediment and organic matter accretion. Although sorption is reversible, sediment and organic matter accretion usually are not (Johnston, 1991).

The ammonia in the sediments was likely retained by sorption and therefore was potentially reversible. Ammonia measured in the sediments decreased from the end of the 1993 year to the beginning of 1994 (Figure 2.4). Unfortuneatly wastewater application had begun about three weeks prior to the June sample collection in 1994. However, if linear accumulation is assumed then sediment concentration increased about 0.106 mg kg^{-1} per day, and the initial concentration was estimated to be about 6 mg kg^{-1}. This initial concentration was considerably lower than the 34.4 mg kg^{-1} at the end of 1993.

A similar reduction was observed in the Natural Wetland and Reference Wetlands between autumn and spring/summer. Ammonia nitrogen in the Natural Wetland sediments decreased from 41.9 mg kg^{-1} in September 1993 to 15.6 mg kg^{-1} in June 1994, while in the Reference Wetlands it decreased from 5.3 mg kg^{-1} to 3.0 mg kg^{-1}, respectively. In September 1994, ammonia nitrogen increased to 20 and 9 mg kg^{-1} in the Natural and Reference Wetlands, respectively. The decrease could be due to microbial processes, and dilution or flushing from the spring runoff. Regardless, sediment

retention capacity was renewed, but ammonia release may have occurred in the spring prior to the start of the experiment.

Assuming the unaccounted for ammonia removal was nitrified/denitrified, then the constructed wetlands should be capable of removing at least 39% of ammonia inputs indefinitely. Alternatively, it could have been incorporated into microbial biomass and not distinguished by measurements of TN in the sediments. Further removal would be dependent on the retention capacity of the wetland sediments. If the sorbed ammonia could be incorporated into microbial biomass and immobilized in the sediments then sediment retention could also be indefinite. Denitrification and organic matter accretion vary with wetland age. As the wetland ages in the first decade or so these processes tend to increase and then stabilize (Craft, 1997), suggesting ammonia removal could occur at the observed rates indefinitely under similar ammonia loading rates.

2.4 Conclusions

Average ammonia removal rates (*i.e.*, mass reductions) ranged from 42 % to 99 % for Dyke water and 32 % to 96 % for Pond water during the three year study. These rates were comparable with rates reported in the literature (Nichols, 1983, Knight et al., 1985, Watson et al, 1989). These removal rates varied depending on ammonia nitrogen loading rates (Figure 2.1). Year 1 (1992) had a relatively low loading rate that resulted in a high treatment efficiency (*i.e.*, percent removal). Year 2 (1993) had a very high loading rate that resulted in a low treatment efficiency. Year 3 (1994) had an intermediate loading rate that resulted in an intermediate treatment efficiency.

Ammonia loading rates ranged from 1.8 to 7.9 kg/ha/d. Assuming 1994 water chemistry conditions, loading rates should not exceed 3 kg N/ha/d to maintain effective removal (*i.e.*, about 70 % mass removal and an outflow concentration of < 2 mg N/L). Loading rates and outflow concentrations observed in other studies ranged from 0.1 to 26.4 kg N/ha/d and 0.2 mg L^{-1} to 48 mg L^{-1}, respectively (Hammer and Knight, 1994). Hammer and Knight (1994) suggest that loading rates should not exceed 3 - 5 kg N/ha/d to produce outflow concentrations of < 4 mg N/L. Removal rates for Pond water tended to be lower than those for Dyke water; however, similar rates were not expected due to the higher contaminant load (*e.g.*, hydrocarbons, suspended solids) in the Pond water.

The dominant removal pathways were suspected to be sediment retention and nitrification/denitrification. In 1994, all removal pathways were measured for Dyke water. Ammonia removal to the sediment and tissue storage pools accounted for about 49 % and 2 % of total removal, respectively. Ammonia removal via volatilization (as measured) accounted for less than 1 % of total removal. Although volatilization may have been underestimated due to the field methodology, it is not likely that ammonia removal via volatilization exceeded 3 % of the total ammonia removed based on predicted rates. Although the measured *in situ* denitrification rates only accounted for 4 % of the total ammonia removed, it is likely that nitrification/denitrification was a dominant removal mechanism.

Although ammonia removal was dependent on input load, the observed ammonia concentrations in the outflow water were within the range predicted in several models. Ammonia was effectively removed by constructed wetlands receiving oil sands wastewater when compared with other free-surface wetlands, despite the other constituents in the wastewater (*i.e.*, hydrocarbons) and being situated at a northern latitude. Observed data were comparable with or better than predicted data from the model representing ammonia removal in free-surface wetlands.

Table 2.1 Experimental design for the Constructed Wetlands study, 1992-1994.

Trench Number	Treatment Water	Design Flow Rate (L/min)	Hydraulic Loading Rate (cm/d)	Duration	
				Start	Stop
		Study Year 1992			
1,4,8	Control[a]	2	1.6	June 29	Sept. 27
2,6,9	Dyke	2	1.6	June 29	Sept. 27
3,5,7	Pond	2	1.6	June 29	Sept. 27
		Study Year 1993			
1,4,8	Control[b]	6	4.9	June 19	Sept. 28
2,6,9	Dyke	6	4.9	June 4	Sept. 28
3,7	Pond	6	4.9	June 19	Sept. 28
5	Pond	6	4.9	June 19	Aug. 9
		3	2.5	Aug. 9	Sept. 1
		0	0	Sept. 1	Sept. 28
		Study Year 1994			
1,4,8	Control[b]	2	1.6	May 18	Sept. 28
2,6,9	Dyke	2	1.6	May 18	Sept. 28
3W[c]	Dyke	4	6.6	June 8	Aug. 15
		1[d]		Aug. 15-18	Sept 28
3E[c]	Dyke	8	13.2	June 8	Aug. 15
		1[d]	1.6	Aug. 15-18	Sept. 28
5W[c]	Dyke	1	1.6	June 2	Sept. 28
5E[c]	Dyke	0.5	0.8	June 2	Sept. 28
7W[c]	Dyke	2	3.3	June 2	Sept. 28
7E[c]	Dyke	0.25	0.4	June 2	Sept. 28

a In 1992 water from a ditch parallel to the study site was used, which was a mixture of surface runoff, ground water and possibly dyke drainage water (*i.e.*, Dyke water).

b In 1993 and 1994, the ditch was not used because of the possible influence of Dyke water. The source was changed to the south mine drainage pond (*i.e.*, Loon Lake) which meets water quality guidelines to be released to the Athabasca River.

c Split trenches were combined (*i.e.*, inputs and outputs were summed) for each trench for discussion as divider integrity was questionable. Sediment and tissue chemistry, denitrification and volatilization were not measured in the split trenches.

d Trench 3W and 3E received phosphate additions. Trench 3W was also aerated.

Table 2.2 Ammonia-, nitrite-nitrate- and total kjeldahl nitrogen concentrations (mean) for the inflow water (A) and outflow water (D) of the constructed wetlands trenches.

Year	Treatment Water	Station	Nitrogen (mg L^{-1})		
			Ammonia	Nitrite-nitrate	Total Kjeldahl
1992	Control	A	0.21	0.96	1.7
		D	0.09	0.03	1.2
	Dyke	A	11.4	6.0	12.6
		D	0.15	0.15	1.3
	Pond	A	10.1	1.2	12.1
		D	0.25	0.15	1.9
1993	Control	A	0.01	0.07	0.42
		D	0.01	0.07	0.87
	Dyke	A	15.9	0.45	18.8
		D	11.9	0.20	15.3
	Pond	A	13.3	0.07	18.1
		D	10.4	0.44	14.9
1994	Control	A	0.001	0.002	0.4
		D	0.001	0.0004	0.6
	Dyke	A	14.6	0.008	16.2
		D	3.7	0.1	3.9

Table 2.3 Ammonia removal in constructed wetlands receiving oil sands wastewater.

Year/ Water	Ammonia Inputs (mean ± SD)		Ammonia Outputs (mean ± SD)		Removal (% of inflow)	Load Removed ($mg\ m^{-2}\ d^{-1}$)
	$mg\ L^{-1}$	$mg\ m^{-2}d^{-1}$	$mg\ L^{-1}$	$mg\ m^{-2}d^{-1}$		
1992						
Dyke	11.6±2.8	185	0.17±0.17	2	99	183
Pond	10.7±3.7	187	0.44±0.41	7	96	180
1993						
Dyke	16.2±3.3	787	11.8±2.0	455	42	332
Pond	13.2±3.8	607	10.9±2.9	412	32	195
1994						
Dyke	14.6±3.0	271	3.7±2.5	65	76	206

Table 2.4 Nutrient sediment chemistry ($mg\ kg^{-1}$) in the constructed wetlands trenches, September.

Year	Treatment Water	Exchangeable Nitrogen		TC	TN	TP	TN:TP
		NH_4^+	NO_3^-				
1993	Control	3.4	nm[a]	43000	1320	nm	nm
	Dyke	34.4	nm	38000	1220	nm	nm
	Pond	38.8	nm	36200	1090	nm	nm
1994	Control	2.11	0.06	40500	1690	249	6.6
	Dyke	20.1	0.10	36500	1275	230	5.5

a nm = not measured

Table 2.5 Concentration of nutrients in plant tissue chemistry (mean) in the constructed wetlands trenches.

Species	Year	Treatment Water	Tissue Type	Total Nitrogen (%)	Total Phosphorous (mg kg^{-1} dry weight)
Cattail	1993[a]	Control	shoot	0.67	nm[c]
			root	1.01	nm
		Dyke	shoot	0.77*	nm
			root	1.43*	nm
		Pond	shoot	0.83*	nm
			root	1.64*	nm
	1994[b]	Control	shoot	1.31	1308
			root	0.69	1578
		Dyke	shoot	1.37	1154
			root	1.36*	1478
Bulrush	1993	Control	shoot	0.78	nm
			root	1.20	nm
		Dyke	shoot	0.97	nm
			root	2.22*	nm
		Pond	shoot	0.85	nm
			root	2.27*	nm
	1994	Control	shoot	1.42	1508
			root	0.93	1726
		Dyke	shoot	1.45	1537
			root	1.90	2306

a September 21, 1993
b August 17, 1994
c nm = not measured
* asterisk indicates statistically different from the Control (α = 0.05) for total nitrogen

Table 2.6 Ammonia nitrogen mass balance (kg trench^{-1} season^{-1}) for Dyke and Pond water.

Parameter	1992		1993		1994
	Dyke[a]	Pond[a]	Dyke[b]	Pond[c]	Dyke[d]
Input (loading) kg ammonia N trench^{-1} season^{-1}	2.9	3.0	16.0	12.3	6.3
Nitrification/Denitrification[e] kg ammonia N trench^{-1} season^{-1}	nm	nm	nm	nm	0.19
Volatilization[e] kg ammonia N trench^{-1} season^{-1}	nm	nm	nm	nm	0.004
Sediment Storage kg ammonia N trench^{-1} season^{-1}	nm	nm	4.48	5.05	2.35
Storage kg N trench^{-1} season^{-1}	nm	nm	-0.4	0.2	0.10
Total Removal Processes[f] kg N trench^{-1} season^{-1}	-	-	4.1	5.2	2.6
Calculated Output[g] kg N trench^{-1} season^{-1}	-	-	11.9	7.1	3.7
Actual Output[h] kg ammonia N trench^{-1} season^{-1}	0.04	0.11	9.2	8.4	1.5
Unmeasured Treatment[i] kg N trench^{-1} season^{-1}	2.9	2.9	2.7	-1.3	4.3

a after 90 days of wastewater application: 1 kg trench^{-1} season^{-1} = 63 mg m^{-2} d^{-1}
b after 116 days of wastewater application: 1 kg trench^{-1} season^{-1} = 49 mg m^{-2} d^{-1}
c after 101 days of wastewater application: 1 kg trench^{-1} season^{-1} = 57 mg m^{-2} d^{-1}
d after 133 days of wastewater application: 1 kg trench^{-1} season^{-1} = 43 mg m^{-2} d^{-1}
e as measured *in situ*
f The sum of all removal to storage pool (sediments and uptake by plants) and by processes (volatilization and nitrification/denitrification).
g Input minus total removal processes; that is, the output load expected based on the measured removal processes.
h The actual output load measured.
i The difference between the calculated output and actual output. Positive values indicate all removal processes were not measured (*i.e.*, treatment was underestimated). Negative values indicate removal processes measured overestimated treatment.

nm not measured

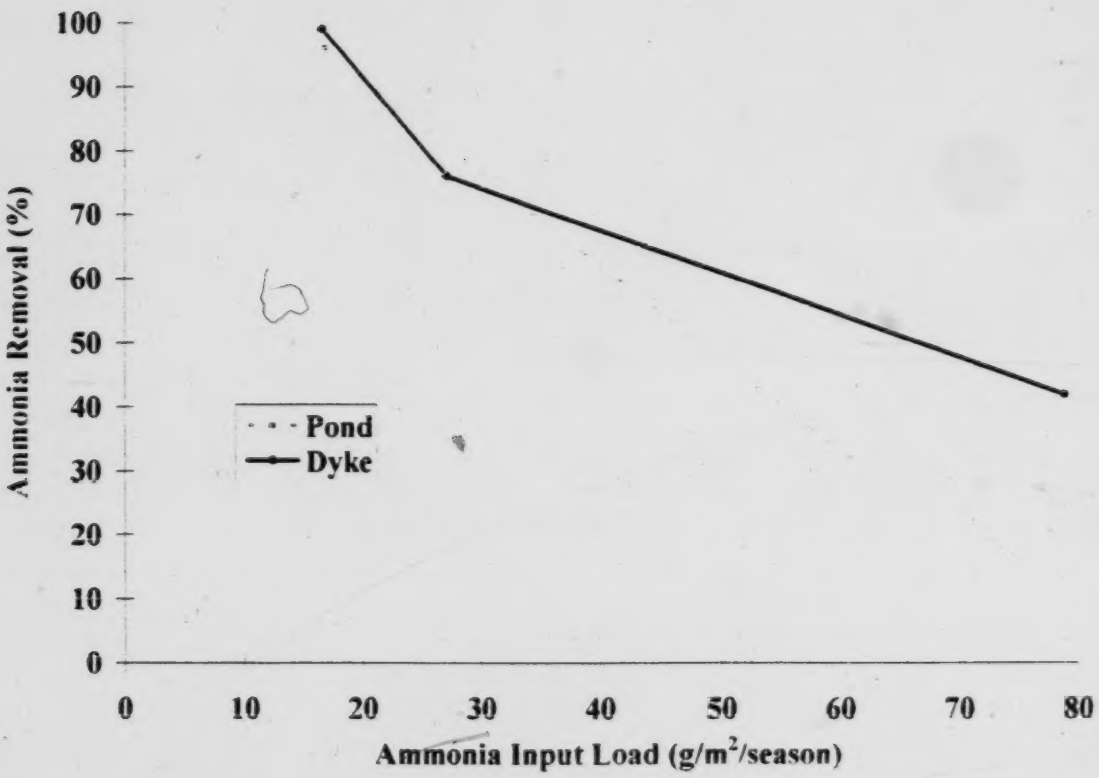


Figure 2.1 Ammonia removal (%) for Dyke (1992 - 94) and Pond (1992 - 93) water.

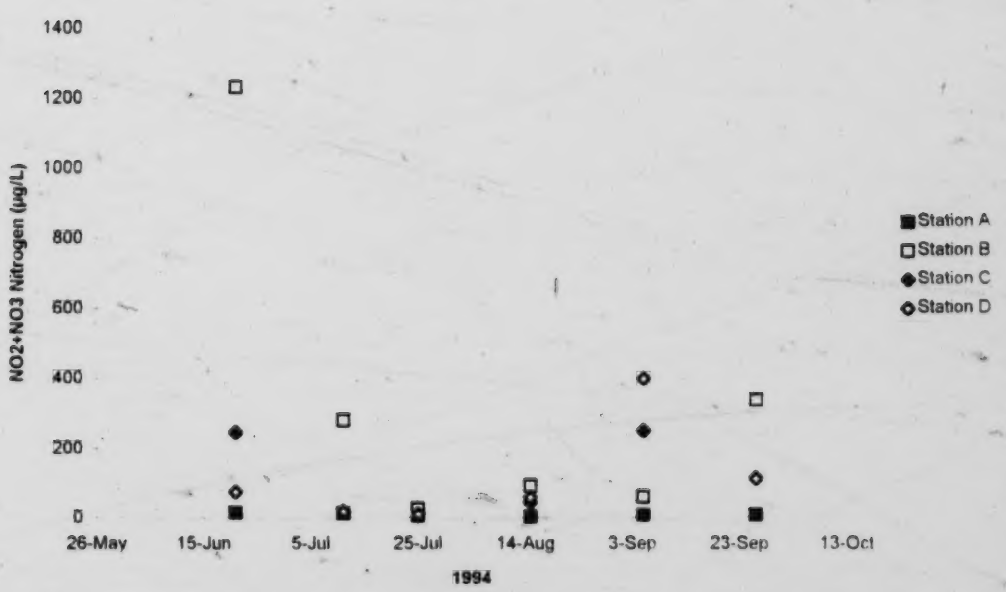
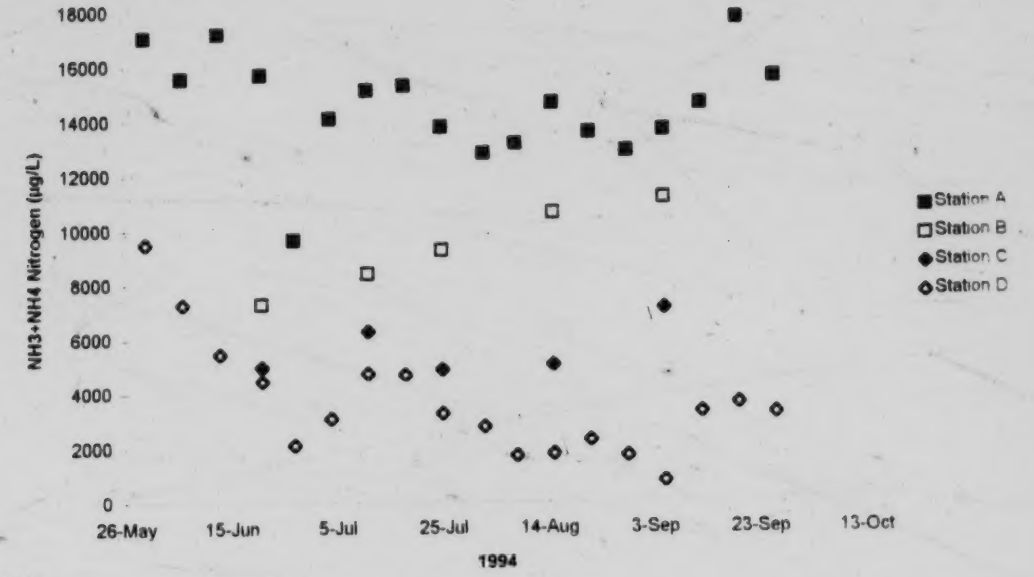
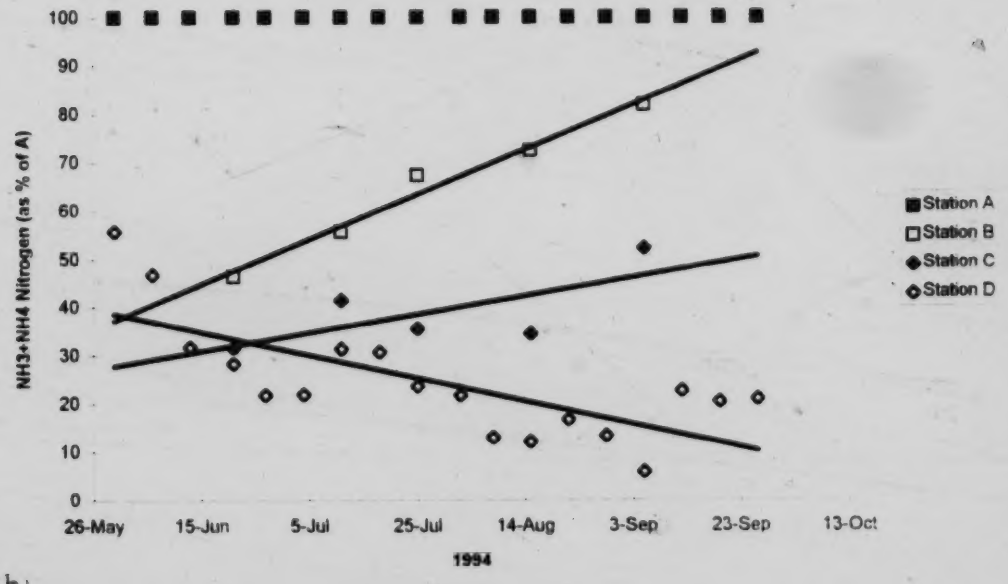


Figure 2.2 Nitrite-nitrate nitrogen concentration in the Dyke water replicate trenches at Stations A, B, C and D, 1994.



(a)



(b)

Figure 2.3 Ammonia-ammonium nitrogen in the Dyke water replicate trenches at Stations A, B, C and D, 1994. (a) concentration, (b) as a % of concentration at Station A

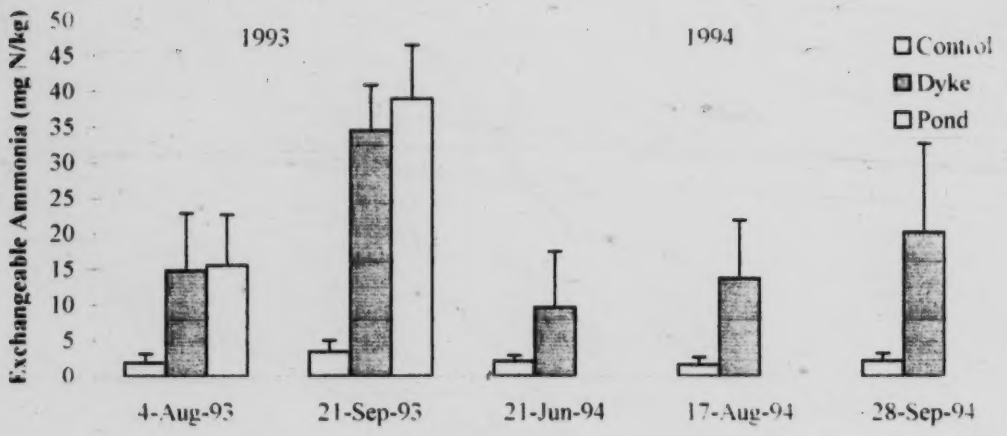


Figure 2.4 Exchangeable ammonia nitrogen (mean ± SD) in the sediments of the constructed wetlands trenches, 1993 and 1994: by date.

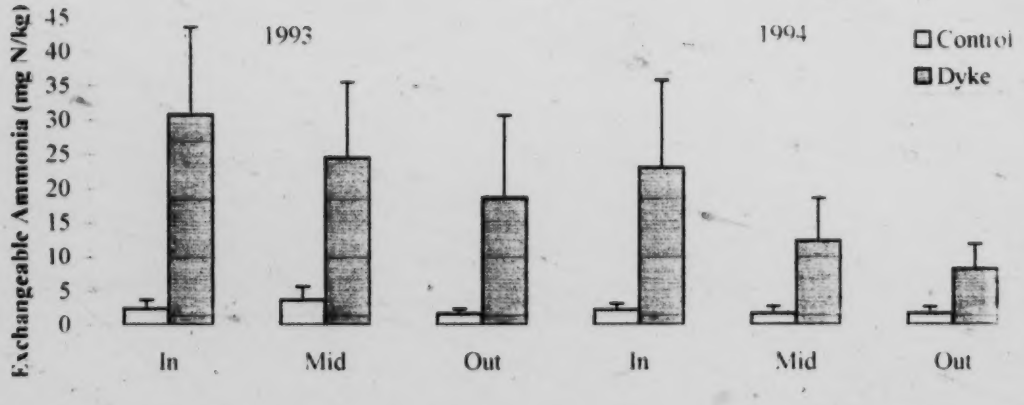


Figure 2.5 Exchangeable ammonia nitrogen (mean ± SD) in the sediments of the constructed wetlands trenches, 1993 and 1994: by zone.

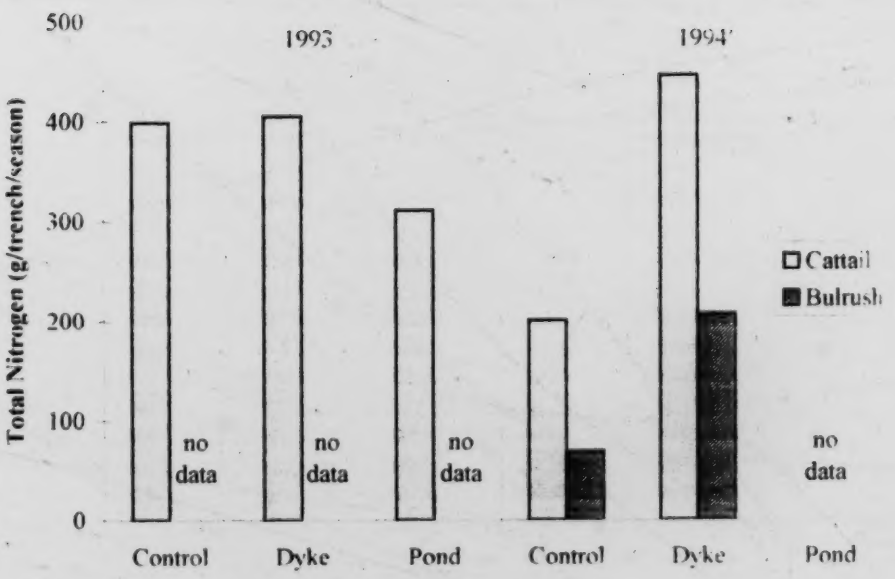


Figure 2.6 Total nitrogen in the storage pool in 1993 and 1994 at the end of the growing season (September).

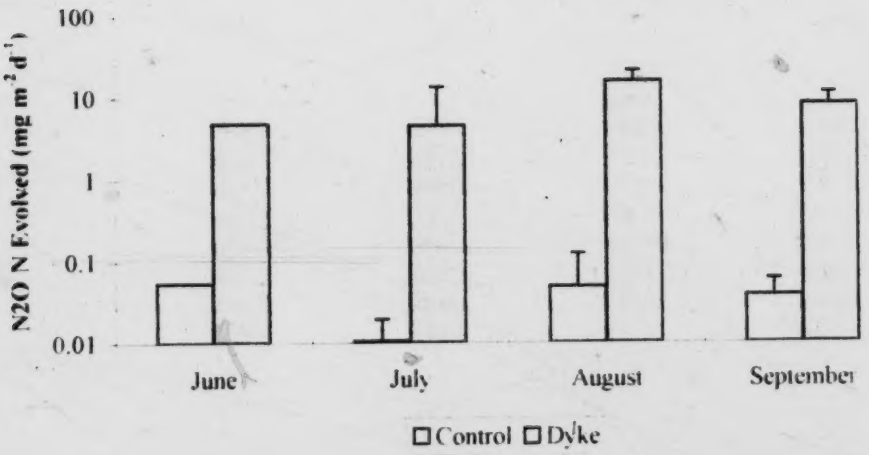


Figure 2.7 *In situ* denitrification (mean ± SD) measured using the acetylene blockage technique in Control and Dyke Drainage trenches, 1994.

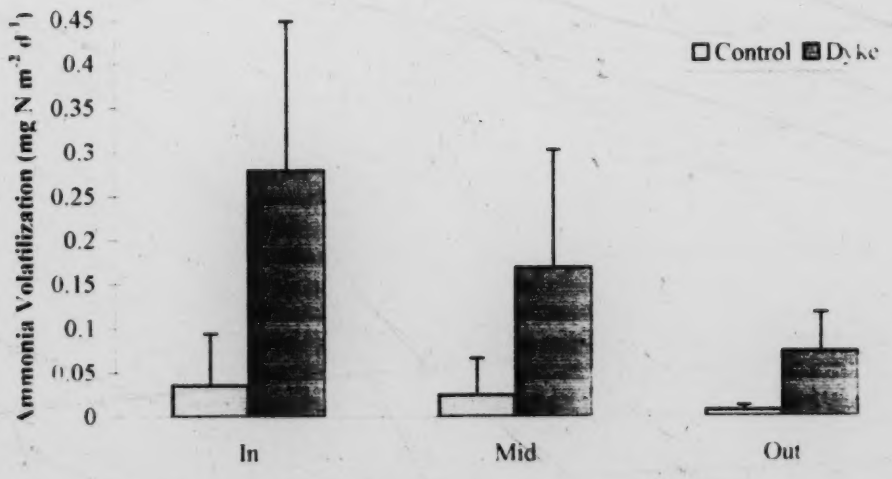


Figure 2.8 Ammonia volatilization rates (mean ± SD) from the Constructed Wetlands trenches, 1994.

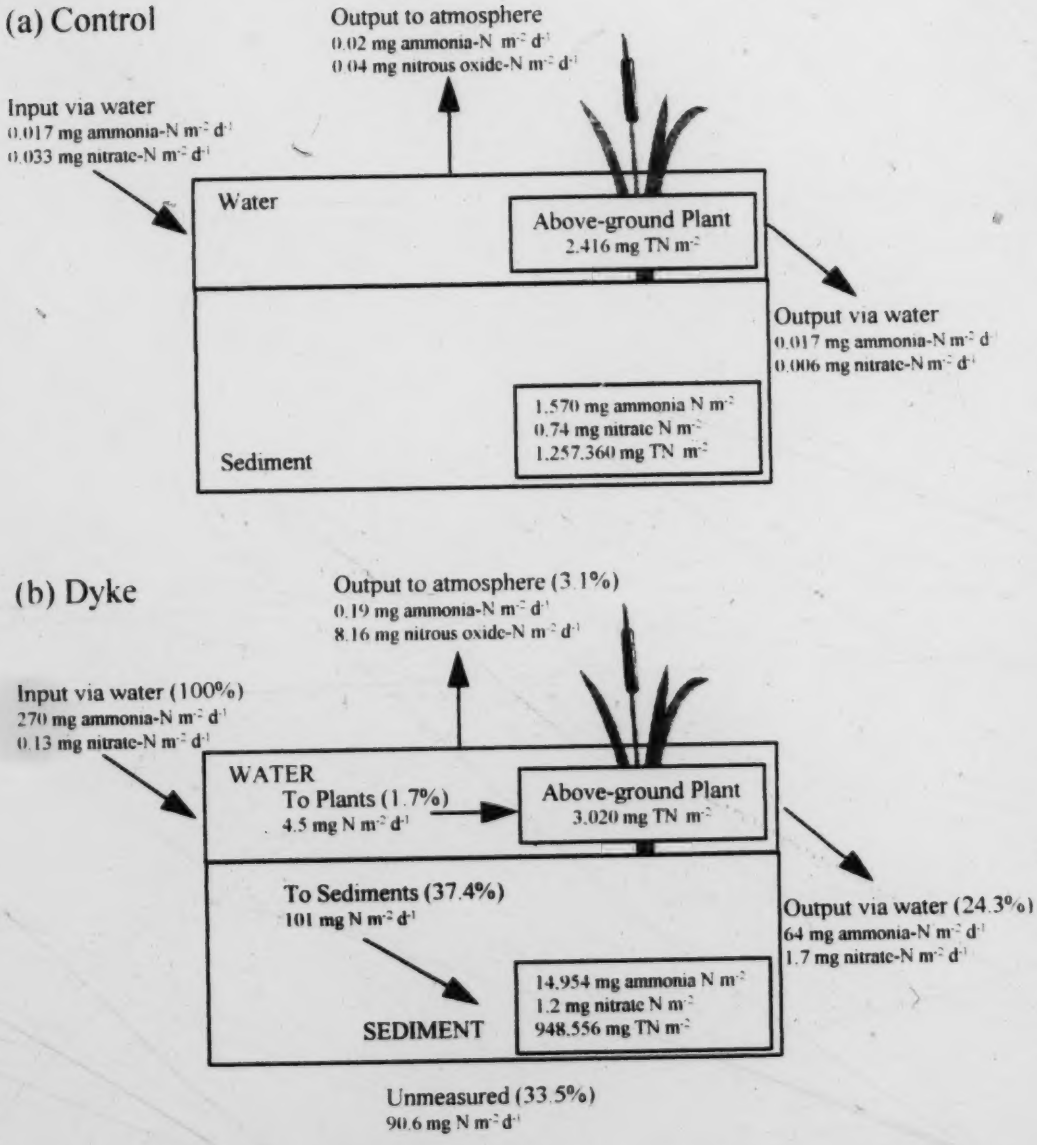
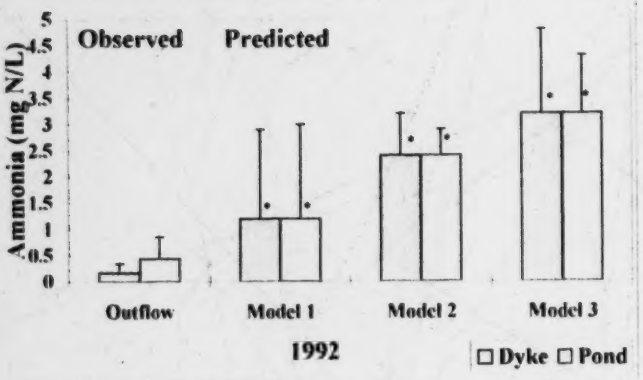
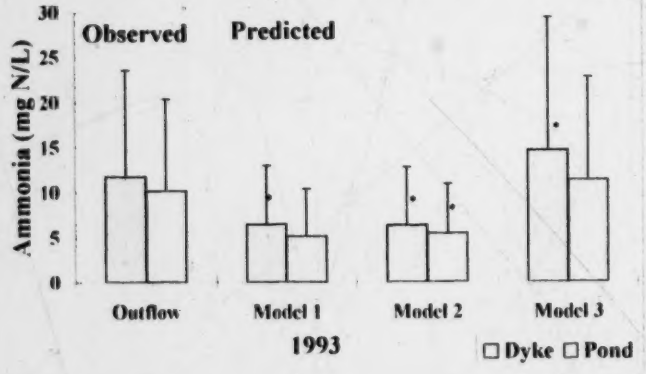
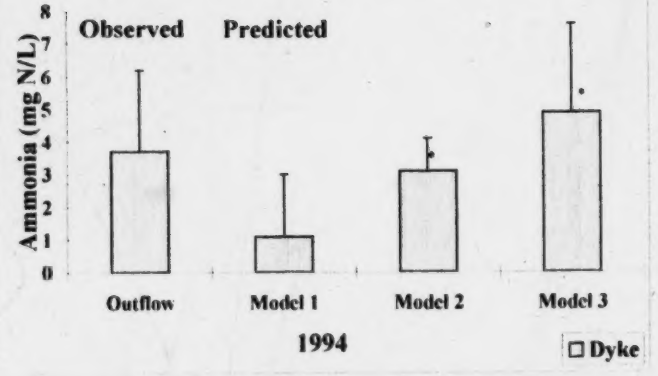


Figure 2.9 The nitrogen budget in the (a) Control and (b) Dyke trenches in 1994. Boxed quantities are mass stored (mg m^{-2}); other quantities are fluxes (mg m^{-2} d^{-1}); number in brackets is percent of input nitrogen.







Model 1 - (Reed et al., 1995): Is based on nitrification rates and includes concentration, temperature and hydraulic retention time (HRT).

Model 2 - (WPCF, 1990): Is based on nitrification rates, but does not include temperature or HRT, although hydraulic loading rate is included.

Model 3 - (Hammer and Knight, 1994): Is based on the performance of 17 free surface wetlands to remove ammonia.

* - significantly different from the observed outflow concentration ($p < 0.05$)

Figure 2.10 Observed and predicted effluent ammonia concentrations (mean ± SD), 1992-1994.

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3.0 HYDROCARBON REMOVAL IN CONSTRUCTED WETLANDS RECEIVING OIL SANDS WASTEWATER

3.1 Introduction

Significant sources of energy are currently obtained from mining of oil-rich sands in northern Alberta (currently more than 15 % of Canada's annual oil needs). Active mining leases during this study were about 26,600 ha, which produced about 300,000 barrels of oil per day (bpd). Recent approvals for new mines include development of another 18,400 ha. Should all mines that are currently proposed become active more than 49,000 ha would be disturbed. These surface mining processes disturb large areas of the landscape which will require reclamation. Additionally, the extraction process produces large volumes of waste tailings that contain various hydrocarbons and ammonia. This study provides a pilot experiment using constructed wetlands to mitigate the environmental impacts of oil sands mining.

Suncor Inc. Oil Sands Group (Suncor) is mining oil sands in northeastern Alberta, Canada, 25 km north of Fort McMurray. The mining and subsequent conversion of oil sands bitumen to synthetic crude oil began in 1967. The Clark Hot Water Extraction Process used to extract bitumen from the oil sands produces a waste tailings. These tailings, made up of sand, clay, water and unrecovered bitumen, are stored in large tailings ponds (Figure 1.2). One component of tailings, the fine clays known as fine tails, dewater very slowly. Therefore, there is potential for the release of contaminated water as leachate and/or surface run-off to terrestrial and/or aquatic systems as these tailings ponds are reclaimed.

A treatment system will be required to mitigate any environmental impact of leachate and/or run-off water. Both organic (*e.g.*, hydrocarbons) and inorganic (*e.g.*, ammonia) contaminants are of concern. A wetlands treatment system was investigated for its potential for sustainability over the long term and subsequent low cost. Leachate from saturated tailings pond sand dykes (hereafter referred to as Dyke water) and tailings pond top water (hereafter referred to as Pond water) were treated in a pilot field-scale facility.

A variety of physical, chemical and biological processes within wetlands are responsible for removing contaminants. However, there are only a few

examples of wetlands being used specifically to treat wastewaters from petrochemical facilities or other sources of organic chemical wastes (Hamilton et al., 1993). The primary contaminants in this wastewater are naphthenic acids and ammonia. However, the focus of this paper is naphthenic acid removal.

Naphthenic acids originate from petroleum crude oil and oil sands bitumen reserves (Fan, 1991; AEP, 1996). Mono- and poly-cycloalkane (cyclohexane and cyclopentane) carboxylic acids with aliphatic side chains of various lengths predominate in this group. Naphthenic acids with 2 rings predominate oil sands tailings (Lai et al., 1995). Naphthenic acids have properties associated with surfactants and this is thought to be one of the factors contributing to the low settling rates of oil sands tailings (AEP, 1996).

Naphthenic acids are of concern because they are toxic and corrosive (Morales et al., 1993). Compounds in the acid fraction of < 1000 molecular weight precipitation at pH of 2.5 account for 80 - 90 % of the total acid fraction which accounts for 55 - 100 % of the toxicity observed in oil sands wastewater (MacKay and Verbeek, 1993). This fraction has been identified as naphthenic acids (Morales et al., 1993).

Naphthenic acids are difficult to analyze by conventional mass spectrometric (MS) techniques because of their polarity and increasing non-volatility with increasing molecular weight techniques (Morales et al., 1993). Although there have been improvements (such as Fast Atom Bombardment Mass Spectrometry), these methods are still not ideal for quantitative analyses of complex mixtures (Morales et al., 1993). Fourier Transform Infrared (FTIR) Spectroscopy has been mainly used for qualitative analysis although recently usage for quantitative analysis has increased. In fact, a quantitative method was developed for measuring naphthenic acids by Syncrude Canada Ltd.; however, this was not available until 1995.

In this study, a method was required that could quantify the naphthenic acids input to and output from the wetlands. As MS techniques utility were limited and expensive and the FTIR method was not available, a surrogate for naphthenic acids that could be quantified was required. Total extractable hydrocarbons (TEH) were analyzed as a surrogate for naphthenic acids. The chromatograph of commercial grade naphthenic acids

and oil sands wastewater were similar and exhibit the same characteristic broad peak between C15 and C28 (Figure 3.1).

A variety of physical, chemical and biological processes in wetlands may act to translocate and transform hydrocarbons. In wetlands receiving hydrocarbons, these processes may act together to effectively remove hydrocarbons from the water column (*i.e.*, retain hydrocarbons such that outflow water quality is improved). Physical, chemical and biological translocation processes include: particulate settling, diffusion of dissolved forms, sorption of soluble forms on substrate, volatilization and plant uptake. It is important to realize that these processes have opposite/countervailing processes which may return hydrocarbons to the water column (*e.g.*, resuspension, litter fall, diffusion). There are also transformation processes that may remove hydrocarbons (*e.g.*, mineralization via microbial degradation) from the water column (Kadlec and Knight, 1996).

It is important to understand the translocation and transformation processes acting to remove chemicals of environmental concern when designing treatment wetlands systems (Kadlec and Knight, 1996). That is, are the contaminants simply retained in the wetlands (*e.g.*, sequestered in sediments or plants) and potentially available to return to the water column, rather than removed from the system (*e.g.*, photolysis, volatilization, mineralization). If contaminants are not removed they may be released back into the water column later, therefore reducing wetland treatment. The expected removal mechanisms are microbial transformation and sedimentation translocation processes; although plant uptake may also contribute to hydrocarbon removal it is not expected to be significant.

Indigenous microbial communities have degraded naphthenic acids (Herman et al., 1994; Lai et al., 1996). Nutrients and temperature were shown to affect biodegradation rates (Lai et al., 1996). Wetlands provide more suitable habitat for microbial communities compared with tailings ponds because of increased surface area and nutrient rich resources; consequently, biodegradation is expected to occur in wetlands.

Other removal mechanisms include volatilization, sedimentation and plant uptake. Naphthenic acids are non-volatile (Morales et al., 1993) and therefore photolysis and volatilization is probably not a significant removal pathway (AEP, 1996). Sedimentation with solids is possible, while organics may also be taken up by plants (Simonich and Hites, 1995).

Although it was expected that hydrocarbon removal would occur in constructed wetlands receiving oil sands wastewater, contaminant fate and treatment efficiency were unknown. Hydrocarbon mineralization by microbial processes occur optimally at specific temperatures; however, actual removal rates may be slowed by the northern latitude (57°N) of the study site. Additionally, there may be competition for resources (*e.g.*, oxygen, phosphorus) from bacteria nitrifying ammonia which is also present in oil sands wastewater.

The objectives of the current study were to determine:

- hydrocarbon removal rates; and
- the fate of the hydrocarbons removed.

3.2 Methods

The general approach involved the monitoring of nine (9) constructed wetlands trenches over a three year period. Hydrocarbon removal rates were estimated by measuring the change in input and output concentrations of total extractable hydrocarbons and water flow. Contaminant fate was assessed by measuring TEH input/output loads and changes in sediment storage.

3.2.1 Site Description and Experimental Design

Experimental Facility

The Suncor experimental constructed wetlands are located in northeastern Alberta, Canada, 25 km north of Fort McMurray (57°04'N 111°28'W). They are located southwest of Tailings Pond 2 between the tailings pond and Highway 63 (Figure 1.1). They were constructed in May and June 1991 and cover an area of approximately 1.4 ha (Figure 1.3). Nine trenches were constructed in 1991 with the following characteristics:

- cell dimensions - 50 m by 10 m at the top and 2 m at the bottom
- side slope - 2:1
- trench slope - 0.5 % (equivalent to a drop of 0.25 m over 50 m)
- mean depth - 0.35 m

- area - 175 m^2
- water volume - 52.5 m^3 (based on 50 m x 3.5 m x 0.35 m x 0.9 porosity)
- liner - 40 mil high density polyethylene
- substrate - 0.45 m of sand topped with 0.15 m of organic muskeg soil
- vegetation - 300 *Typha latifolia* (cattail) shoots and 60 *Scirpus validus* (bulrush) culms (bearing 6 - 15 shoots) were planted in each trench in June 1991
- establishment - 1 year

Experimental Design

Treatment waters were applied to the nine trenches in a randomized block design. Three replicate Control trenches were compared with treatment trenches (Dyke or Pond). The experimental design changed (*i.e.*, flow rates) from year to year (Table 2.1).

Monitoring Programme

There were two sampling schemes depending on the type of analysis: 1) four sampling stations from inflows to outflows (*i.e.*, A, B, C, D) was followed for water quality and water chemistry, and 2) three stations from inflows to outflow (*i.e.*, in, mid, out) was followed for sediment chemistry. For the four station sampling scheme, Station A samples were taken from the inflow pipes, Station B was located 15 - 17 metres downstream of the inflow to each trench, Station C 30 - 34 metres downstream of the inflow, and Station D samples were taken from the outflow pipe/weir (50 m downstream of the inflow). For the three station sampling scheme, "in" samples were collected from within the first third (0 - 15 m) of each trench, the "mid" from the second third (16 - 30 m) and the "out" from the last third (31 - 45 m).

Sample frequency was limited in 1992 due to water limitations (*i.e.*, water was transported by truck in 1992 rather than pumped as in 1993 and 1994). In 1993 and 1994, water chemistry was sampled as frequently as weekly to ensure that the sample frequency was at least as often as trench turnover (*i.e.*, within the estimated mean hydraulic retention time of 7 to 18 days). Sediment sample frequency was once per study year.

3.2.2 Sample Collection

Water

Water samples were collected directly into sample bottles and shipped to the laboratory (ASL in Vancouver, BC) the same day such that sample analysis was initiated within a seven day holding time.

Sediment

Sediment samples were collected using a plastic corer (5 cm in diameter) with only the top 1 cm being collected. Several grab samples were collected at each station and placed in "whirl pack bags" to ensure a minimum of 100 g of sample.

3.2.3 Sample Analysis

The analysis of Total Extractable Hydrocarbons (TEH) was conducted in accordance with USEPA Method 3510/8015 (USEPA, 1984). The procedure involved the extraction with methylene chloride. The extract was then reduced in volume and analyzed by capillary column gas chromatography with flame ionization.

3.2.4 TEH Budget

TEH were measured in sediments during 1993 and 1994. Mass balance equations were determined by estimating the inputs, outputs and sediment storage.

The following mass balance equation can be applied to processes determining the fate of contaminants within wetlands:

$$inputs = outflow + mineralization + volatilization \pm change\ in\ storage$$

Depending on the compartments and processes measured, this equation can be rewritten to estimate the unknown compartment/process.

3.2.5 Statistical Analysis

3.2.5.1 Water Chemistry

The water chemistry data were not statistically analyzed because of low sample numbers at inflow stations (*i.e.*, composites were taken from the three replicate trenches to reduce costs) and a lack of variation (as many Control samples results were less than the detection limits). Data were graphically interpreted to assess whether there was a difference between treatment waters or from inflow to outflow for a given wastewater.

3.2.5.2 Sediment Chemistry

Sediment concentration (mg kg^{-1}) data were tested for significant difference amongst treatment waters. All statistical analyses were performed using the SYSTAT statistical package (Wilkinson, 1990). A probability of $\alpha \leq 0.05$ was used to define statistical significance.

Repeated measures analysis of variance (ANOVA) tests were conducted on the TEH concentrations in sediments to assess the effects of wastewater type. Individual trenches were used as replicates of the treatment water type (*i.e.*, the treatments were sampled in triplicate). Measurements were replicated three times in each sampling period (*i.e.*, date) or zone (*i.e.*, in, mid, out) for most sediment data. Repeated measures design is the same as a split plot design, with the treatments applied to the whole plots or trenches and the sampling period and zone applied within plots or trenches (*i.e.*, the trenches were replicates for testing treatments, but blocks for testing sampling period or zone effects). No trench effects were assumed. Post-hoc contrasts were used to determine which means were significantly different using Bonferroni adjusted alpha levels (*i.e.*, critical level of 0.05 divided by the number of contrasts tested). Testing a subset of comparisons rather than all possible pairwise comparisons (*e.g.*, Tukey HSD) often gives more power to the analysis (Wilkinson, 1990). Repeated measures ANOVAs were conducted for each parameter (*e.g.*, total nitrogen in bulrush root, exchangeable ammonia in sediments, *etc.*) and year separately (*i.e.*, 1993 and 1994).

3.3 Results and Discussion

3.3.1 Water Chemistry

In all study years TEHs in the water were reduced from inflow to outflow in the Dyke and Pond trenches while they stayed about the same for Control trenches (Table 3.1). Control inflow concentrations were about an order of magnitude lower than in Dyke or Pond inflows (except in 1992 when Ditch water was used). Dyke inflow concentrations were in the range of 13 to 37 mg L^{-1}, and Pond inflow concentrations were in the range of 12 to 46 mg L^{-1}. Control inflow concentrations were generally < 4 mg L^{-1}, except in 1992 when Ditch water rather than Loon Lake water was used. On average the inflow concentrations of Dyke and Pond water were lower in 1992 compared with 1993 and 1994, following the same trend observed for ammonia (Chapter 2). Average Dyke outflow concentrations were in the range of 4 to 27 mg L^{-1}, and Pond outflow concentrations were in the range of 8 to 26 mg L^{-1}. Control outflow concentrations were generally < 1.5 mg L^{-1}.

3.3.2 TEH Removal

TEH removal occurred in both the Dyke and Pond trenches; however, removal varied from year to year. In 1992, removal efficiency was in the range 69 - 76 %; however, in 1993 and 1994 the efficiency was lower presumably because of increased contaminant loading.

TEH removal efficiency decreased as loading increased for a given wastewater stream (Figure 3.2). However, Pond water, which had a higher load, had higher removal rates than Dyke water (Table 3.2). Since Pond water has a high sediment load to which TEHs could bind, the higher removal may have been due to the reduction in TEH associated with the solids. This suggests that TEH removal rates may vary depending on the predominant removal mechanism.

Hydrocarbon removal has been reported in the literature; however, instead of using TEH as a measure of petroleum hydrocarbons, oil and grease was used. The oil and grease method does not differentiate between natural and anthropogenic hydrocarbon sources as well as the TEH method (Nix et al., 1993). Although removal rates were determined by differences in oil and grease rather than TEH, the removal rates were considered comparable

with this study. Direct concentration comparisons are not appropriate, but a comparison of removal efficiency is useful. Oil and grease removal efficiency reported in the literature ranged between 53 % to 96 % (Table 3.3). This efficiency was higher than the efficiency observed in this study. However, input loading rates for the literature studies were lower than in this study, suggesting that the lower removal efficiencies reported in this study were due to the higher input loading rates.

3.3.3 Sediment Chemistry

Total extractable hydrocarbon concentrations were lower in the sediments of the Control trenches than either the Dyke and Pond trenches except in 1993 for Dyke trenches (Table 3.4). However, these trends were not significantly different in any year. No significant trends in the sediments from inflow to outflow were observed.

3.3.4 TEH Mass Balance

The mass balance for TEH in the constructed wetlands treatment trenches was determined for each study year (Table 3.5). TEH input and output loading and change in the sediment storage compartment were measured, and from this information a mass balance in Dyke and Pond trenches was calculated. Other processes that could have contributed to hydrocarbon removal include volatilization, plant uptake and microbial mineralization. These processes were not measured in this study.

Removal to the sediments accounted for 8 - 27 % of the TEH retained. The unaccounted TEH load could have been volatilized, taken up by plants or mineralized by microbes. Volatilization was not expected to be significant because naphthenic acids were expected to make up the majority of TEH and these compounds are not readily volatilized (Morales et al., 1993). Although plant uptake and microbial mineralization were not measured in this study, parallel studies were conducted in these same constructed wetlands trenches to assess these potential removal mechanisms (Nix et al., 1994 and 1995).

The parallel studies found little or no TEH uptake by the emergent aquatic macrophytes (hereafter referred to as macrophytes) which make up the majority of the plant biomass (Nix et al. 1994 and 1995). In the parallel studies, carbon dioxide (CO_2) production was measured as an indicator of

mineralization. The final product of complete biodegradation (*i.e.*, mineralization) of hydrocarbons is CO_2. Nix et al. (1994 and 1995) modified a method used to measure CO_2 production rates from soils (Anderson, 1982). In 1994, about 6.8 kg C/wetlands/season (as CO_2) was measured leaving the Dyke trenches; however, only 1.9 kg C (or 2.2 kg TEH assuming carbon made up 85 %) were retained by the wetlands (*i.e.*, the inflow load minus the outflow load). This suggests that the CO_2 evolved from the trenches represents other processes in addition to mineralization of hydrocarbons.

The amount of CO_2 evolved from the Dyke and Pond trenches was corrected by CO_2 evolved from or respired in the Control trenches, to account for any processes other than TEH mineralization. However, the difference due to nitrification/denitrification would not have been included in this "correction" as elevated ammonia only existed in Dyke and Pond trenches. In 1994, about 3.6 kg ammonia N were retained by the trenches (not including what was retained by the sediments or macrophytes), which would produce 4.6 kg C assuming the unaccounted for ammonia was nitrified/denitrified. Subtracting this carbon due to nitrification/denitrification from the total evolved means about 2.2 kg C was evolved due to mineralization which is about equal to the unaccounted for carbon retained (*i.e.*, 1.9 kg C) by the trenches. This, means that the corrected CO_2 evolved from Dyke and Pond trenches was close to the sum of CO_2 produced from nitrification/denitrification and TEH mineralization.

In 1993, however, there were much lower CO_2 evolution rates (Nix et al., 1994). Mineralization did not seem to contribute substantially to hydrocarbon retention by the trenches once the above consideration for nitrification/denitrification was included. It seems unlikely that the difference could be made up by losses via volatilization. The primary removal mechanisms were likely mineralization and sedimentation, but the contributions from each could not be calculated from the available data.

3.4 Conclusions

Average TEH removal rates (*i.e.*, mass reductions) ranged from 19 % to 76 % for Dyke water and 54 % to 69 % for Pond water during the three year study. These rates were lower than rates for oil and grease reported in the literature (Table 3.3). The difference was probably due to the amount of contaminant loading. Input loading was on average higher in this study and ranged from 146 to 1143 mg m^{-2} d^{-1} compared with 32 to 168 mg m^{-2} d^{-1}

for oil and grease in the other studies. TEH removal rates varied by year. Year 1 (1992) had a relatively low loading rate which resulted in a high treatment efficiency. Year 2 (1993) had a very high loading rate which resulted in lower treatment efficiency than in 1992. Year 3 (1994) had an intermediate loading rate which resulted in an intermediate loading rate for Dyke water.

TEH removal to the sediments accounted for less than 30 % of the TEH load retained by the wetlands in this study. Other removal mechanisms include volatilization, plant uptake and microbial mineralization. Volatilization was not expected to be significant and parallel studies did not indicate plant uptake was significant and the removal via mineralization was unclear. Further method development is required to ensure removal processes and storage are reflected accurately. Although the fate of TEH remained unclear, removal was substantial and warrants further investigation to assess the role of constructed wetlands in the oil sands industry with respect to hydrocarbon treatment and reclamation.

Table 3.1 Total extractable hydrocarbon in water (mg L^{-1}) for the inflow (A) and outflow (D) of the constructed wetlands trenches.

Year	Treatment Water	Station	Min	Max	Mean	SD
1992[a]	Control	A	1.1	8.3	6.2	3.3
		D	< 1	4.1	1.3	1.1
	Dyke	A	10.6	18.3	13.8	3.6
		D	1.4	5.9	4.0	1.5
	Pond	A	5.4	21	12.2	7.0
		D	4.2	11.1	7.9	2.8
1993[b]	Control	A	< 1	2.1	0.9	0.6
		D	< 1	3.4	1.2	1.0
	Dyke	A	7.5	30.7	20.4	8.6
		D	5.3	54	20.8	14.1
	Pond	A	6.4	75.2	46.0	28.2
		D	9.0	66.4	25.7	16.0
1994[c]	Control	A	< 1	26.5	3.5	8.1
		D	1	2.6	1.3	0.4
	Dyke	A	25.6	46.8	37.6	6.1
		D	10.7	38.7	27.5	6.5

a samples were collected 4 times in 1992; trench inflows were composited (n=4) and outflows were individual samples (n=12)

b samples were collected 6 times in 1993; trench inflows were composited (n=6) and outflows were individual samples (n=12)

c samples were collected 9 times in 1994; trench inflows were composited (n=9) and outflows were individual samples (n=27)

Table 3.2 Total extractable hydrocarbons (TEH) removal in constructed wetlands receiving oil sands wastewater.

Year/ Water	TEH Inputs (mean ± SD)		TEH Outputs (mean ± SD)		Removal (% of inflow)	Load Removed ($mg\ m^{-2} d^{-1}$)
	$mg\ L^{-1}$	$mg\ m^{-2}\ d^{-1}$	$mg\ L^{-1}$	$mg\ m^{-2}\ d^{-1}$		
1992						
Dyke	13.8	220	4.0	52	76	168
Pond	12.2	211	7.9	65	69	146
1993						
Dyke	20.4	992	20.8	799	19	193
Pond	46	2116	25.7	973	54	1143
1994						
Dyke	37.6	696	27.5	484	30	212

Table 3.3 Oil and grease removal in various wetlands treatment facilities.

Input Load[a] ($mg\ m^{-2}\ d^{-1}$)	Inflow $mg\ L^{-1}$	Outflow $mg\ L^{-1}$	Removal (%)	Reference
32	2.1	0.130	94	Litchfield, 1993
168	0.840	0.290	65	Dong and Lin, 1994
-	12.6	0.490	96	Ramirez, 1993
113	4.3	2.0	53	Duda, 1992

a calculated from information given; information to calculate output loading was not given

\- no information given to calculate input loading

Table 3.4 Total extractable hydrocarbons in the sediments (mg kg^{-1}) in the constructed wetlands trenches.

Year	Treatment Water	Mean	SD	n
1992	Control	1250	1084	12
	Dyke	2076	2932	12
	Pond	1275	1172	12
1993	Control	1402	1087	9
	Dyke	1141	973	8
	Pond	1618	1858	9
1994	Control	953	830	3
	Dyke	1247	150	3

Table 3.5 Total Extractable Hydrocarbon mass balance for Dyke and Pond water.

Parameter	1992		1993		1994
	Dyke[a]	Pond[a]	Dyke[b]	Pond[c]	Dyke[d]
Input (loading) kg TEH/wetlands/season	3.5	3.3	20.1	37.4	16.2
Total Removal Processes[e] Sediment Storage kg TEH/wetlands/season	nm	nm	2.5	3.5	2.7
Calculated Output (Input - Removal)[f] kg TEH/wetlands/season	-	-	17.6	33.9	13.5
Actual Output (untreated load in outflow)[g] kg TEH/wetlands/season	0.8	1.0	16.2	17.2	11.3
Underestimated treatment performance[h] kg TEH/wetlands/season	-	-	1.4	16.7	2.2

a after 90 days of wastewater application: 1 kg trench^{-1} season^{-1} = 63 mg m^{-2} d^{-1}

b after 116 days of wastewater application: 1 kg trench^{-1} season^{-1} = 49 mg m^{-2} d^{-1}

c after 101 days of wastewater application: 1 kg trench^{-1} season^{-1} = 57 mg m^{-2} d^{-1}

d after 133 days of wastewater application: 1 kg trench^{-1} season^{-1} = 43 mg m^{-2} d^{-1}

e The sum of all removal to storage pool (sediments and uptake by plants) and by processes (volatilization and nitrification/denitrification).

f Input minus total removal processes; that is, the output load expected based on the measured removal processes.

g The actual output load measured.

h The difference between the calculated output and actual output. Positive values indicate all removal processes were not measured (*i.e.*, treatment was underestimated).

nm not measured

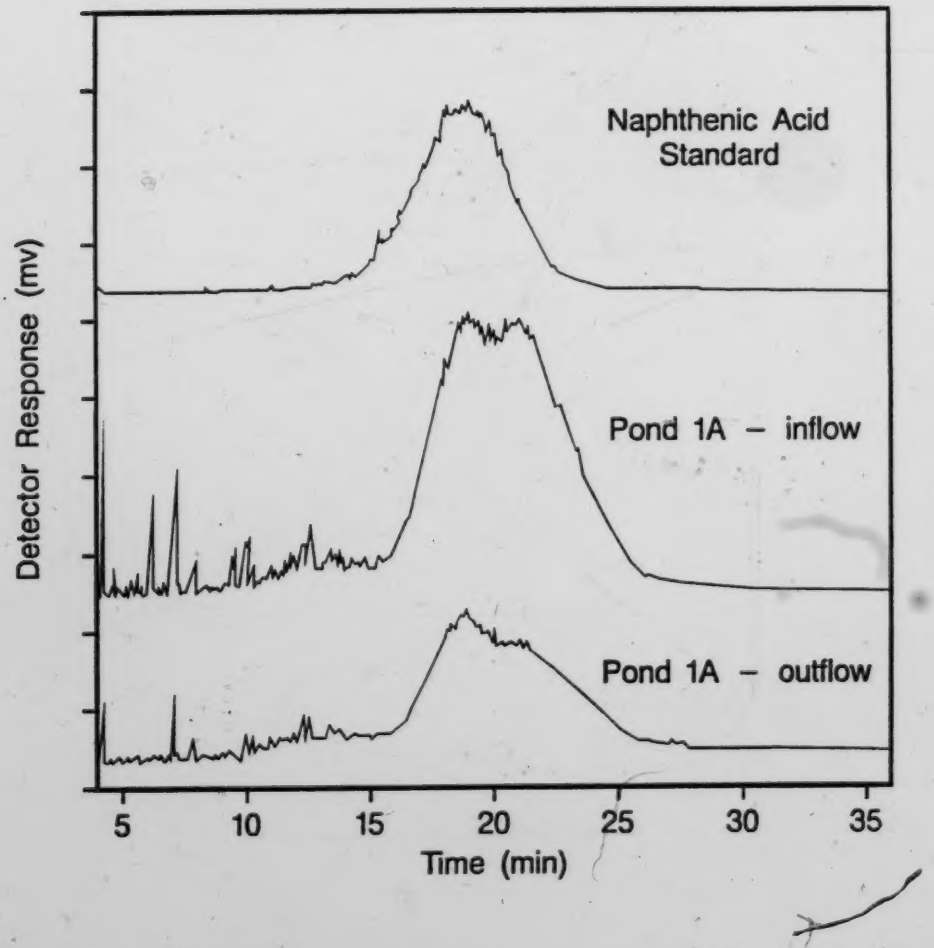

Figure 3.1 A comparison of GC chromatograms for a naphthenic acid standard and Pond inflow and outflow water. (Nix et al., 1993)

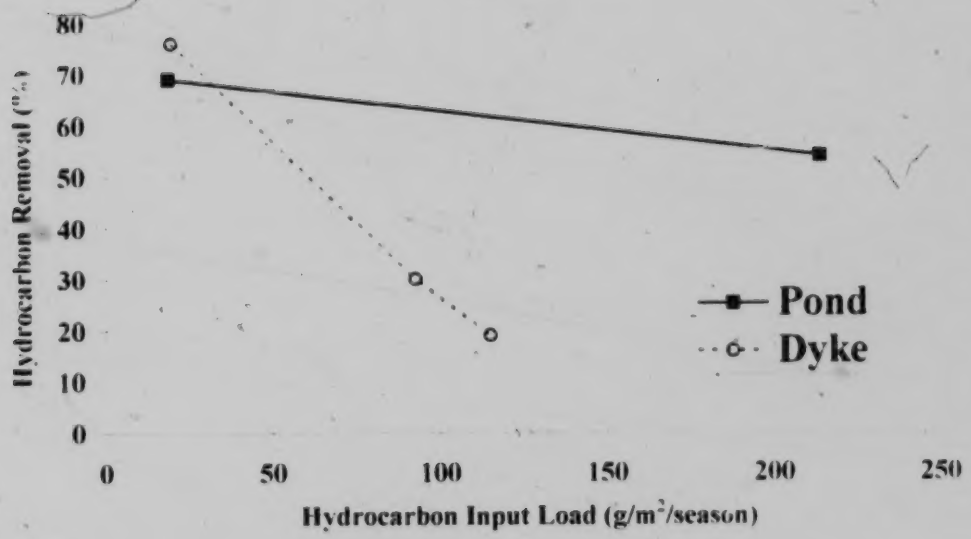

Figure 3.2 Hydrocarbon removal (%) for Dyke (1992 - 94) and Pond water (1992 - 93).

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4.0 EMERGENT AQUATIC MACROPHYTE PRODUCTION AND DECOMPOSITION IN CONSTRUCTED WETLANDS RECEIVING OIL SANDS WASTEWATER

4.1 Introduction

Significant sources of energy are currently obtained from mining of oil-rich sands in northern Alberta (currently more than 15 % of Canada's annual oil needs). Active mining leases during this study were about 26,600 ha, which produced about 300,000 barrels of oil per day (bpd). Recent approvals for new mines include development of another 18,400 ha. Should all mines that are currently proposed become active more than 49,000 ha would be disturbed. These surface mining processes disturb large areas of the landscape which will require reclamation. Additionally, the extraction process produces large volumes of waste tailings that contain various hydrocarbons and ammonia. This study provides a pilot experiment using constructed wetlands to mitigate the environmental impacts of oil sands mining.

Suncor Inc., OSG is currently mining oil sands in north eastern Alberta, Canada, 25 km north of Fort McMurray. The bitumen (*i.e.*, oil) is extracted from the oil sands by the Clark Hot Water Extraction process (Gulley and Klym, 1992). Fine tailings, a by-product of the process, is made up of clay, water and unprocessed bitumen, and is stored in tailings ponds on the Suncor lease. Wastewater associated with these ponds must be detoxified as part of the reclamation scheme(s) for the Suncor site. Preliminary evidence supports the potential use of wetlands to treat some of these wastewaters. A wetland that established accidentally in dyke seepage from a tailings pond reduced contaminant concentration and toxicity from inflow to outflow (Hamilton and Nix, 1992).

The ecological consequences of using constructed wetlands to treat oil sands wastewater were investigated. Aquatic macrophytes (hereafter referred to as macrophytes) have direct and indirect effects on contaminant removal and treatment efficiency, as well as being potential indicators of ecosystem health. Macrophytes can remove contaminants by direct uptake, and/or provide the necessary environment for physical removal mechanisms and habitat for microbial removal mechanisms. Macrophyte production and decomposition play direct and indirect roles in improving water quality, and therefore they were studied to understand

the viability and sustainability of constructed wetlands receiving oil sands wastewater.

Macrophytes have the ability to directly remove contaminants by metabolic and absorption processes. Plant metabolism (both biosynthesis and catabolic reactions) of refractory organics, bacteria and virus; and plant absorption of nitrogen, phosphorus, metals and refractory organics are direct removal processes which may occur in wetlands treatment systems (Watson et al., 1989). Macrophytes have been shown to take up metals (*e.g.*, Kadlec and Tilton, 1979; Morea et al., 1990; Wood and McAtamney, 1994, *etc.*) and nutrients (*e.g.*, Gersberg et al., 1984, 1987; Nichols, 1983; Rogers et al., 1991; Tanner et al., 1995). The role of plants in metal removal is secondary to sedimentation (Dunbabin and Bowmer, 1992), and their role in nutrient removal is often secondary to microbial and sedimentary processes. However, under specific conditions nutrient uptake by plants may be the primary removal mechanism (*e.g.*, Rogers et al., 1991). Although the contribution of plant uptake to overall removal is generally low, macrophytes are important because they enhance removal by other processes.

Macrophytes indirectly affect contaminant removal in wetlands receiving wastewater. Macrophytes stabilize sediments with their roots and rhizomes, which prevents erosion (Dunbabin and Bowmer, 1992). They also disperse flow, further reducing the threat of erosion and channelization. Concomitantly, sedimentation rates are increased as water velocity is reduced (Dunbabin and Bowmer, 1992). Macrophytes (live and dead biomass and leaf litter) provide a surface for degrading/mineralizing bacteria (*i.e.*, biofilm). Macrophytes also increase the oxygen transfer to the sediments by oxidizing the rhizosphere. This oxygen transfer supports aerobic microbial populations in the rhizosphere (Brix, 1990). These microbes modify nutrients, metals and trace organics which often results in their removal from the wastewater (Gersberg et al., 1986). Nitrogen can be removed to the atmosphere by nitrifying/denitrifying bacteria (Hammer and Knight 1994). Metals precipitate to the sediments with hydrogen sulphide, produced by sulphate reducing bacteria (Faulkner and Richardson, 1989), while organics are mineralized by bacteria. These modifying microbes require nutrients which can be obtained through the decomposition of macrophytes which recycles nutrients back into the system. Regardless of whether macrophytes play a direct or indirect role in contaminant removal their contributions to wastewater treatment cannot be overlooked.

Production and decomposition of macrophytes are important processes in a healthy wetland. In order for the macrophyte community to provide habitat for bacteria and other organisms, take up nutrients and oxygenate the sediments, healthy, viable vegetation must be maintained. Decomposition of annual dieback vegetation must also be maintained to recycle nutrients back into the system thereby providing the necessary resources for the microbial community that degrades contaminants. Hence macrophyte production and decomposition was used as a measure of wetland sustainability in this study.

The objective of this study was to determine the deleterious impacts of oil sands wastewater on macrophyte production and decomposition in constructed wetlands. The null hypotheses tested were: 1) no difference in macrophyte production in constructed wetlands trenches receiving different test waters, and 2) no difference in macrophyte decomposition in constructed wetlands trenches receiving different test waters. Nitrogen dynamics and nitrogen and hydrocarbon retention by the constructed wetlands were addressed in separate chapters (Chapters 2 and 3, respectively).

4.2 Methods

4.2.1 Site Description and Experimental Design

Experimental Facility

The Suncor experimental constructed wetlands are located in northeastern Alberta, Canada, 25 km north of Fort McMurray (57°04'N 111°28'W). They are located southwest of Tailings Pond 2 between the tailings pond and Highway 63 (Figure 1.1). They were constructed in May and June 1991 and cover an area of approximately 1.4 ha (Figure 1.3). Nine trenches were constructed in 1991 with the following characteristics:

- cell dimensions - 50 m by 10 m at the top and 2 m at the bottom
- side slope - 2:1
- trench slope - 0.5 % (equivalent to a drop of 0.25 m over 50 m)
- mean depth - 0.35 m
- area - 175 m^2

- water volume - 52.5 m^3 (based on 50 m x 3.5 m x 0.35 m x 0.9 porosity)
- liner - 40 mil high density polyethylene
- substrate - 0.45 m of sand topped with 0.15 m of organic muskeg soil
- vegetation - 300 *Typha latifolia* (cattail) shoots and 60 *Scirpus validus* (bulrush) culms (bearing 6-15 shoots) were planted in each trench in June 1991
- establishment - 1 year

The trenches were planted with *Typha latifolia* (10 cattail shoots per 6 m^2) and *Scripus* sp. (2 bulrush culms of 6 - 15 shoots each per 6 m^2) in early June 1991, and allowed to establish for the remainder of the 1991 growing season. These planting densities were similar to those used in other studies (*e.g.*, Cooper and Hobson, 1989; Van Oostrom and Cooper, 1990; Pullin and Hammer, 1991). *Typha latifolia* was selected because *Typha* spp. are hardy, widespread, easy to grow, and are capable of surviving under adverse environmental conditions (Desjardins et al., 1986; McNaughton et al., 1974). *Scirpus validus* was selected due to its superior (to *Typha* spp.) ability to translocate oxygen to the roots (Gersberg et al., 1986). In addition, both plants were selected because they inhabited the area prior to wetland construction. Donor sites (with limited impacts from the industrial site) were easily located on the Suncor mine lease.

Experimental Design

Treatment waters were applied to the nine trenches in a randomized block design. Three replicate Control trenches were compared with treatment trenches (Dyke or Pond). The experimental design changed (*i.e.*, flow rates) from year to year (Table 2.1).

In addition to the constructed wetland trenches, an adjacent contaminated wetland (called the Natural Wetland) and four reference wetlands were monitored. The Natural Wetland was located adjacent to the constructed wetlands system and received unknown amounts of Dyke Drainage water from Pond 2 as well as inputs from surface runoff water. Over the three study years four different reference wetlands were monitored (Figure 4.1). Together these wetlands provided information on or about longer term impacts and natural variability.

Monitoring Programme

Three stations, per trench, from inflow to outflow (*i.e.*, in, mid, out) were sampled. The "in" samples were collected from within the first third (0 - 15 m) of each trench, the "mid" from the second third (16 - 30 m) and the "out" from the last third (31 - 45 m). Sample frequency varied depending on the study year and is described below.

4.2.2 Production

In 1992, trenches were sampled only in August, while in 1993 and 1994 they were sampled in July, August and September. Net primary production was estimated by measuring peak above-ground standing crop. The experimental design for the production measurements varied somewhat year to year (Table 4.1). Three to five 0.25 or 1 m^2 quadrat plots per zone were harvested. In 1992, 1 m^2 quadrat plots were used, but later as vegetation became more dense, quadrat number and size were reduced to three 0.25 m^2 in 1993 and 1994.

Live above-ground tissues were clipped at the soil surface in each plot, and plants were sorted into three groups for later drying and weighing: cattail, bulrush and all other species. When possible, plants were identified using Moss (1983), Niering (1989) and Weinmann et al. (1984).

Below-ground biomass was sampled only in the September survey in 1993 and 1994. In 1993, a coffee can (15 cm diameter; 17 cm depth) was used as a corer. One end of the can had been removed while several holes had been put into the other end. Once the above-ground vegetation had been removed the corer was placed in the centre of the plot and pushed into the sediment using a spade to separate the corer and its contents from the surrounding sediment and roots. The complete recovered core was stored under cool conditions until sieved. Upon sieving, biomass was sorted into current years and older growth for both cattail and bulrush, and other biomass was lumped together. New rhizome growth was relatively easy to differentiate from older growth, unless rhizomes were discoloured by the anoxic sediments, at which time differentiation became somewhat subjective. Wet weights were measured and the samples were then dried at ~40°C and weighed again. Since results were highly variable in 1993, in 1994 a less labour intensive sampling method was used. Single shoots were collected

(above- and below- ground parts). Above- and below- ground parts were separated. Old growth (*i.e.*, growth occurring in previous years) was removed from below-ground parts.

Biomass samples were dried at 40°C to a constant weight and weighed using an electronic Mettler balance to the nearest 0.1 g or 0.001 g depending on total weight (*i.e.*, if less than ~ 160 g then weighed to 0.001 g) to obtain both above- and below-ground dry weights. This information was also used for nitrogen budget calculations (Chapter 2).

In addition to destructive biomass sampling, water depth, number of cattail and bulrush shoots, and the presence of other species was recorded for each plot. Also, the number of cattail infloresences were counted for each zone rather than per plot.

4.2.3 Decomposition

Decomposition was assessed using litter bags made of fibre glass window screening (Davis, 1991) exposed for various periods throughout 1992 to 1994 (see Table 4.2 for experimental design). The window screening was sewn into "litter bags" approximately 10 x 12 cm with monofilament line. Each bag was weighed and filled with 4 g (1992) or 1 g (1993/94), dried and chopped leaves (approximately 0.5 to 2 cm in length to standardize surface area), to the nearest 0.001 g. Green leaves were used in 1992 and 1993 (after Bayley et al., 1985; Nelson et al., 1990a and 1990b). However, weight loss was much higher than many studies reported in the literature because of the difference in litter quality. Standing dead leaves were used in 1994 (after Bruquetas de Zozaya and Neiff, 1991; Davis, 1991) to address this. The bags were tied to stakes and allowed to float for the first few days until they became water logged and settled to the sediment surface. New litter bags were placed in the trenches each year. One set of replicate bags from each station at each site were removed periodically after initial placement. Upon retrieval, the bags were rinsed to remove blue-green algae, various invertebrates, and roots and shoots that had penetrated or covered the bags. Bags were then dried to a constant weight at 40°C and weighed on an electronic Mettler balance to the nearest 0.001 g.

4.2.4 Statistical Analysis

Production data (biomass/m^2) were logged [*i.e.*, log(biomass+1)] following convention for biological data containing zero values to produce approximate normal distribution (Zar, 1984). Decomposition data (as percent of weight lost during exposure period) were arcsin square root transformed following convention for percent data (Zar, 1984). All statistical analyses were performed on the transformed data using the SYSTAT statistical package (Wilkinson, 1990). A probability of $\alpha \leq 0.05$ was used to define statistical significance.

Repeated measures analysis of variance (ANOVA) was conducted on the constructed wetlands data set, to assess the effects of wastewater type. However, 1992 data were not of repeated measures design and were treated as one-way ANOVA design. Although there were three to five replicates (*e.g.*, quadrats or litter bags) for each zone within each sampling period these individual data points were not used, but rather the means of these data were used. It is valid to conduct these statistical analyses over means especially if there are missing data (Hudson, pers. comm.). Missing data were especially prevalent for the decomposition data set in the longer exposure periods. Individual trenches were used as replicates of the wastewater type. Measurements were replicated three times in each sampling period (*i.e.*, date) or zone (*i.e.*, in, mid, out). The treatments (*i.e.*, wastewater type) were sampled in triplicate and these same replicates (*i.e.*, trenches) were also sampled repeatedly over time (*i.e.*, number of sampling periods) and space (*i.e.*, three zones within each trench). Repeated measures design is the same as a split plot design, with the treatments applied to the whole plots or trenches and the sampling period and zone applied within the plots or trenches (*i.e.*, the trenches were replicates for testing treatments, but blocks for testing the sampling period and zone effects). No trench effects were assumed.

Post-hoc contrasts were used to determine which means were significantly different using Bonferroni adjusted alpha levels (*i.e.*, critical level, 0.05, divided by the number of contrasts tested). Testing a subset of comparisons rather than all possible pairwise comparisons (*e.g.*, Tukey's HSD) often gives more power to the analysis (Day and Quin, 1989; Wilkinson, 1991).

4.3 Results and Discussion

4.3.1 Production

Comparison Among Treatments

Total production (*i.e.*, peak above-ground standing crop) varied significantly among treatments in 1993 only (Table 4.3). In 1992, no differences among treatments were detected by one-way ANOVA on the data collected from the constructed wetlands (n = 3; $p > 0.05$). In 1993, cattail above-ground biomass was higher in the Control and/or Dyke Drainage trenches than in the Pond trenches ($F = 5.48$; $p = 0.04$). Bulrush biomass was higher in the Dyke Drainage and/or Pond trenches than in the Control trenches (though not statistically significant). These trends were most evident in September 1993 (Figure 4.1). In addition, above-ground biomass for other macrophytes tend to be greater in the Control trenches than in the Dyke Drainage and/or Pond trenches (though not statistically significant). However, total biomass was not significantly different ($F = 2.157$; $p = 0.197$). And again in 1994, above-ground biomass was not significantly different (*e.g.*, total biomass: $F = 0.305$; $p = 0.59$) between treatments (*i.e.*, water input type).

The lack of difference among treatments suggests that oil sands water was not affecting macrophyte above-ground biomass, although the amount of variability could have masked differences. For example, in 1994 data, *a posteriori* power analysis indicated that between 14 and 51 samples would have been required to ensure only 20 % (*i.e.*, power of 80 %) chance of committing a Type II error (*i.e.*, accepting the null hypothesis when it should not have been accepted). Although trenches were subsampled, there were only three trenches per treatment and a total of 9 samples per trench were collected.

Trends in above-ground biomass were not consistent over all study years. Although in 1993 *Typha latifolia* biomass was higher in the Control trenches than in the Dyke or Pond trenches, and other species biomass also tended to be higher in the Control trenches (although not statistically significant), it is not possible from this study alone to suggest the fate of macrophytes under long term exposure to oil sands wastewater. There were data (though rarely statistically significant) that indicate the potential for lower production and diversity in wetlands receiving wastewater.

Potentially, production of *Typha latifolia* and other species could be higher and *Scirpus validus* lower in the Control trenches compared with Dyke and Pond trenches (*e.g.*, Figure 4.1). Both biomass and number of taxa of other species tended to be higher (though not statistically significant) in the Control trenches. However, the response of lower species richness and the same or higher abundance is a typical community response to environmental pollution (*e.g.*, Pearson and Rosenberg, 1978). This trend in diversity was also observed in the Natural Wetland when compared with the Reference Wetlands. The Natural Wetland was dominated by *Typha latifolia* and *Carex* sp., while several more species were present in the Reference Wetlands. This suggests that treatment wetlands may end up with limited diversity. The impact of decreased diversity on treatment effectiveness/sustainability is unknown. Should constructed wetlands fulfill a reclamation requirement as well as a treatment function, lower macrophyte diversity could impact wildlife usage.

Below-ground Biomass

Below-ground biomass was highly variable and no trends were observed among treatments (Table 4.4).

Variation Between Years

Production between 1992, 1993 and 1994 was significantly different for Control and Dyke trenches. Production of the Control and Dyke trenches tended to be lower in 1994 compared with 1992 and 1993 (F = 17.372; p = 0.001). However, production between 1992 and 1993 was not different for Control, Dyke and Pond trenches.

In 1993, *T. latifolia* mean biomass was 373 g m^{-2} and 265 g m^{-2} in Control and Dyke Drainage trenches, respectively. In 1994, *T. latifolia* mean biomass was 140 g m^{-2} and 176 g m^{-2} in Control and Dyke Drainage trenches, respectively. This same trend of decreased biomass in 1994 (as compared with previous years) was also observed for *S. validus* biomass.

Decreased production over time may affect treatment effectiveness/sustainability and wildlife usage. Production decreased in all constructed wetland trenches between 1993 and 1994. This was attributed to muskrats (rather than application of oil sands wastewater), as muskrats

were observed in all trenches. There was physical evidence of muskrat use of cattail and bulrush shoots. Muskrats are known to cut large amounts of emergent vegetation, primarily cattails (Lacki et al., 1990), and build muskrat "houses" and alter the landscape patterns of wetlands (*e.g.*, Mitsch and Gosselink, 1993) often referred to as "eat-outs" (*e.g.*, Errington et al., 1963). Muskrats can be a major concern with respect to treatment wetlands because they can reduce dense stands of emergent macrophytes (*e.g.*, Berg and Kangas, 1989 found they cut about 20 %) to a patchwork of open water and vegetated areas, and can burrow into dykes, which could lead to system failure (Kadlec and Knight, 1996).

In 1994, muskrats were seen daily. There was evidence of muskrat cuts through the trenches, especially the Control trenches, and the beginnings of muskrat mounds/houses. Muskrats appeared to prefer the Control to the Dyke trenches which were preferred over the old Pond trenches that now received Dyke water, as almost all bulrush and significant number of cattail shoots had been cut from two Control and one Dyke trenches. Although muskrats were regularly trapped and removed to other locales, muskrats were observed in the study area throughout the 1994 study year and by the end of 1994 there was evidence of muskrat cuts in all trenches.

This relatively significant impact on the emergent vegetation did not appear to impact treatment effectiveness. However, if this level of muskrat activity continued treatment could become limited. Therefore, the potential of muskrat activity in any potential constructed wetlands should be considered during wetland design to prevent any reduction in treatment effectiveness over time.

Comparison with Natural Wetlands and Reference Wetlands

Above-ground biomass in the constructed wetlands (334 g m^{-2} to 676 g m^{-2}) was comparable with the biomass observed in the natural wetlands (398 to 691 g m^{-2}) and reference wetlands (242 to 582 g m^{-2}).

Although *Scirpus validus* was present in the adjacent Natural Wetland, the Natural Wetland was dominated by *Carex* spp. and *Typha latifolia*. However, in the constructed wetland trenches, in 1993, *Typha latifolia* tended to predominate in the Control and Dyke trenches, while *Scirpus validus* tended to predominate in the Pond trenches. As the Natural Wetland had

been receiving Dyke water since the mid 1980s, it appears that other factors may impact macrophyte communities in the long term.

Water levels in the Natural Wetland increased about 15 cm in 1991 due to construction of a berm at the outflow end of the Natural Wetland. Since 1991, macrophyte biomass has decreased possibly due to the change in water level, making it difficult to determine if Dyke water may deleteriously impact aquatic macrophytes. While the age of wetlands can also affect the production (Noe et al., 1995) and the reference wetlands were likely older than the Natural Wetland, the production of the Natural Wetland was higher possibly due to nutrient enrichment from subsurface seepage from the adjacent tailings ponds.

Although above-ground biomass decreased over time in the constructed wetland trenches, biomass tended to remain higher than in the Reference Wetlands. Biomass in the Reference Wetlands was generally lower than in oxbow lakes of Athabasca River. The average peak above-ground biomass in oxbow lakes of Athabasca River ranged from 456 to 848 g m^{-2} in 1981 (Lieffers, 1983). One wetland in the 1981 study was the same as used in this study in 1991 (*i.e.*, the Shipyard Lake Reference Wetlands). The average above-ground biomass in 1981 was 456 g m^{-2} (Lieffers, 1983) compared with 373 g m^{-2} in 1991 (this study).

4.3.2 Decomposition

Comparison among treatments

Decomposition (as measured by % weight loss) occurred in all treatments, but tended not to vary significantly among treatments, except in 1993 (Table 4.6). In 1993, decomposition was significantly different between treatments (F = 22.2; p = 0.002), and all treatments differed significantly from one another (F = 37.2; p = 0.001 as determined by post-hoc testing - linear contrast). In 1992, decomposition was lower in Pond trenches than in either the Dyke or Control trenches, but the difference was not significant among treatments (F = 1.14; p = 0.38). In 1994, decomposition was not significantly different among treatments for either *T. latifolia* (F = 0.46; p = 0.55) or *Scirpus validus* (F = 1.41; p = 0.32).

Generally, decomposition tended to decrease from Control to Dyke to Pond trenches (Table 4.5). Although these trends were only significant in 1993

(Figure 4.2), they suggest that leaching and/or bacterial decomposition of leaf litter was retarded under the heavier contaminant loads that occurred in 1993 (*i.e.*, 6 L/min inflow in 1993 compared with 2 L/min in 1992 and 1994). This study could not determine if the reduced decomposition was due to competition for resources (*e.g.*, oxygen, phosphate) or the toxic effects of the contaminants.

In study years where no significant differences were observed among treatments *a posteriori* power analysis was conducted. Ignorance of a study's power can have serious consequences by misleading environmental managers preparing mine closure reclamation plans (Peterman, 1990). Power was low in 1992 and for longer exposure periods (*i.e.*, > 21 days) in 1994. Overall power was acceptable for shorter exposure periods, but not for longer. Between 14 and 51 replicates or more would have been needed to improve power to acceptable levels (*i.e.*, 80 %) for longer exposure periods.

Litter Quality

Several factors can affect decomposition: climate (*i.e.*, temperature, moisture), litter type, oxygen, nutrients and flow. While decomposition is slower under cooler temperatures (Nelson et al., 1990a), temperature effects were not observed in this study and within year differences in temperatures were not tested. Litter quality also affects decomposition rates (Nelson et al., 1990a; Szumigalski and Bayley, 1996). Generally, the higher the nutrient content the faster the rate of decomposition. Szumigalski and Bayley (1996) found that percent weight loss was correlated with N content and C:N ratios (*i.e.*, the greater N the greater the weight loss after 1 and 2 years).

In 1993, decomposition occurred in all treatments at a higher rate than in 1992, while in 1994 decomposition occurred in all treatments at lower rates than in 1993. Litter type was different among study years: green in 1992 and 1993, and standing dead in 1994. Flow was different among study years: 2 L/min in 1992 and 1994, and 6 L/min in 1993. Either of these factors could be responsible for the differences observed.

As there were no differences in climate or litter type between 1992 and 1993, it is possible that the change in decomposition was due to changes in flow or the available nutrients. The increased flow rate may have increased dissolved oxygen. The increased flow in 1993 increased the

contaminant loading which may have increased the demand for oxygen and nutrients, but also may have increased the dissolved oxygen content. Since the decomposition rates increased between 1992 and 1993, it is also possible that the microbial populations were not well established in 1992 compared with 1993 populations, which would have increased decomposition in 1993.

While flow rates affect decomposition, the result varies depending on the wetland examined (Mitsch and Gosselink, 1993). Decomposition may occur more rapidly under periodic flooding (Brinson et al., 1981) or in the mainstream of a river rather than on the wet swamp floor (Brinson, 1977). Under permanently submerged conditions there is better access to aquatic detritivores, a more constant physical environment for the microbiota, a greater availability of dissolved nutrients, and a better environment for leaching (Odum and Heywood, 1978). However, if water is anaerobic biological activity can be significantly reduced (Tupacz and Day, 1990).

Decomposition of *Typha latifolia* was 52 % and 47 % in 1993 for the Control and Dyke trenches, respectively; compared with 19 % and 18 % in 1994. These trends were not tested statistically due to the differences in experimental design. The differences in decomposition between 1993 and 1994 was attributed to the change in litter quality. Standing dead leaves were used in litter bags in 1994 rather than green leaves as in 1993 and 1992. Litter quality of the standing dead leaves is lower (*i.e.*, the proportion of the harder to decompose lignin fraction is higher) than in green leaves. Higher decomposition in green leaves compared with standing dead leaves has been observed elsewhere (Nelson et al., 1990a).

The simple exponential model ($Q/Q_0 = e^{-kt}$) described by Olson (1963) was used to estimate rates of decay. This model is widely used where the relative decay rate remains constant through time assuming easily degraded and recalcitrant materials interact to yield a constant decay rate (Nelson, 1990a). Decay rates and half lives are given in Table 4.5 and can be compared with literature values presented in Table 4.6. Half lives ranged from 39 to 347 days (calculated from decomposition in the first 42 days), and were within the ranged of 29 to 610 days reported in the literature. Nelson (1990a) estimated decay rates for green leaves at about twice the rate as for senesced leaves. In this study the difference was about three times for *Typha latifolia*. Decay rates calculated from data given by Thormann and Bayley (1997) for green *Typha latifolia* leaves in a marsh

north of Edmonton were 0.0154 and 0.0028 after 30 and 365 days, respectively. Decay rates after the shorter period were comparable with 1993 rates in this study suggesting that the difference between years was due to litter quality.

Species Variation

Differences between decomposition rates for *Typha latifolia* and *Scirpus validus* may also be attributed to differences in litter quality. Different decomposition rates for *Typha* spp. and *Scirpus* spp. have been observed in other studies (*e.g.*, Kulshreshtha and Gopal (1982) found that *Scirpus* sp. decay rates were almost twice as fast as for *Typha* sp.). Although the differences between these species were lower, they were likely attributable to differences in litter quality. Nitrogen has been suggested to enhance decomposition rates (Puriveth, 1980; Thormann and Bayley, 1997). *Scirpus validus* tissues tended to have higher nitrogen content than *Typha latifolia* (Chapter 2), suggesting that nitrogen content affected decomposition rates in this study also.

Comparison with Natural Wetland and Reference Wetlands

The trend of higher decomposition in the Control compared with Dyke and Pond water trenches was comparable with the trend of higher decomposition in the Reference Wetlands than in the Natural Wetland (Figure 4.3). Decomposition was significantly lower in the Natural Wetland than the Reference Wetland in 1993 (T = -2.5; p = 0.022), though significant trends were not observed in other years.

Decomposition was also faster in the Reference Wetlands and Natural Wetland compared with the constructed wetland trenches. This difference was likely due to winter temperatures. Water flow to the constructed wetland trenches did not continue throughout the winter and the trenches were allowed to freeze over the winter. However, the Natural Wetland received continuous inputs and did not freeze and it is presumed also that the Reference Wetlands also did not freeze to the sediments.

4.4 Conclusions

Although the potential impacts of oil sands wastewater (*i.e.*, Dyke and Pond water) on aquatic macrophytes are still not well understood, there is

potential that both macrophyte production and decomposition may be negatively impacted by oil sands wastewater. As significant differences were only observed in 1993 (under higher loads), it is possible impacts can be controlled by controlling loading. Additionally, natural impacts such as the effect of muskrats or beavers may significantly affect the success of treatment constructed wetlands. A plan to address them should be included in the design, implementation and operation of treatment wetlands.

The most significant observation is that macrophytes continued to grow and appeared to "thrive" in the oil sands wastewaters after three study years of application. Given the high natural variability in production in wetlands, the effects of climate, muskrat activity and wastewater loading cannot be separated. Macrophyte production tended to be lower in trenches receiving oil sands wastewater, though not significantly. However, the sampling design may have been inadequate due to relatively high variation and a low number of replicates as suggested by the *a posteriori* power analysis. The lack of significant differences suggest no impact; however, the power of the study was low so the potential for accepting the null hypothesis when it was false was high. Larger-scale, longer-term demonstration wetlands are required before implementing treatment wetlands as part of mitigation design/mine closure.

Leaf litter provides surface area and nutrients for bacteria, and therefore can indirectly affect contaminant removal. In addition, decomposition plays an important role in overall wetland function by recycling nutrients. Although trends in decomposition were not statistically significant in all study years, there was some indication that oil sands wastewater could reduce litter decomposition. *A posteriori* power analysis indicated that there were insufficient replication at longer exposure periods, while at shorter exposure periods it was acceptable (*i.e.*, power of 80 %). Differences in decomposition under shorter exposure periods were only detected under the higher loading in 1993. However, the cause of the observed decreased decomposition rates could have been the higher contaminant loads or low dissolved oxygen or some combination.

The impact of reduced macrophyte production and/or decomposition rates on treatment efficiency and sustainability is unknown. In 1994, when the apparent production was substantially reduced by muskrats, wastewater treatment efficiency was not affected (Chapter 2). While no clear trend of contaminant impact on macrophyte production and/or decomposition was

observed, it is important to note that loss of wetland function could limit the use of wetlands as a reclamation option and perhaps also as a treatment option for the oil sands industry. This study suggests that a longer term larger, pilot-scale project is warranted to assess the efficiency of wetland treatment and the sustainability of wetland function.

Table 4.1 Experimental design for production measurements.

Design Feature	1992[a]	1993[b]	1994[c]
Sites	9 CW 1 RW[d] 1 NW	9 CW 2 RW[d] 1 NW	6 CW[e] 3 RW[d] 1 NW
Zones per Site	1[f]	3	3
Quadrats per Zone	1[g]	3	3
Quadrat Size (m^2)	1	0.25	0.25
Quadrat Location Determination	selected[h]	random	random
Sample Periods			
July	-	y	y
August	y	y	y
September	-	y	y
Parameters (frequency sampled)			
Above-ground Biomass	1	3	3
Shoot Density	1	3	3
Shoot Lengths	1	3	3
Shoot Widths	1	-	-
Diversity	-	3	3
Typha latifolia Inflorescences	1	2	3
Below-ground Biomass	-	1	1
Water Depth	-	3	3

CW Constructed Wetlands Trenches
RW Reference Wetlands
NW Natural Wetlands

\- not measured
y measured

a 1992 sample periods: above-ground biomass on July 30-31; other parameters August 10-13

b 1993 sample periods: June 26-July 3; August 1-7; September 1-9; only T7, T8 and T9 were sampled in August (2nd) survey

c 1994 sample periods: July 6-7; August 3-4; September 1-9

d see Appendices A

e split trenches were monitored once in September 1994 for a total of 12 trenches (6 replicate and 6 split)

f 1 for above-ground biomass and 3 for other parameters measured

g 1 for above-ground biomass and 5 for other parameters measured

h selected based on sparse vegetation so large zones selected for shoot density and morphology?; and better established area (@ Station B) selected for biomass to prevent decimation of a particular area

Table 4.2 Experimental design for litter decomposition.

	1992	1993	1994
Sites	9 CW	9 CW 1 RW[a] 1 NW	6 CW 1 RW[a] 1 NW
Zones per Site	3	3	3
Litter Bags per Zone	1[b]	5	5
Initial Placement	August 15	July 24	June 26
Exposure Periods	1[c]	5[d]	3[e]
Species	*Typha latifolia*	*Typha latifolia*	*Typha latifolia* *Scirpus validus*
Type	Green	Green	Senesced
Total Number of Litter Bags	27[b]	825	720

[a] Gravel Pit Reference Wetland see Appendix A
[b] originally placed three bags per zone, but two bags per zone were used for microbiological tests
[c] 41 day exposure period
[d] 21 day, 42 day, 63 day, 290 day, and 438 day exposure periods
[e] 21 day, 42 day, and 84 day exposure periods

Table 4.3 Above-ground macrophyte biomass (mean ± standard deviation) in the constructed wetlands, 1992 - 1994.

Sample Period	Treatment	Above-ground biomass (g dry wt m^{-2}) Cattail	Bulrush	Other	Total
August 1992	Control	-	-	-	450 ± 111
	Dyke Seepage	-	-	-	592 ± 162
	Pond 1A	-	-	-	353 ± 52
	Natural Wetlands	-	-	-	534 ± 148
	Reference Wetlands	-	-	-	373 ± 183
July 1993	Control	140 ± 85	112 ± 87	22 ± 37	275 ± 117
	Dyke Seepage	132 ± 69	84 ± 81	10 ± 31	226 ± 99
	Pond 1A	121 ± 70	120 ± 105	4 ± 13	245 ± 105
	Natural Wetlands	104 ± 98	20 ± 43	129 ± 174	253 ± 174
	Reference Wetlands	37 ± 46	74 ± 66	63 ± 26	174 ± 46
August 1993	Control	397 ± 165	105 ± 204	41 ± 54	544 ± 168
	Dyke Seepage	285 ± 116	153 ± 102	11 ± 32	450 ± 92
	Pond 1A	224 ± 156	162 ± 135	16 ± 47	401 ± 142
	Natural Wetlands	190 ± 189	0 ± 0	144 ± 175	334 ± 219
	Reference Wetlands	36 ± 63	66 ± 58	66 ± 25	169 ± 52
September 1993	Control	373 ± 239	145 ± 141	67 ± 93	585 ± 243
	Dyke Seepage	265 ± 169	158 ± 146	47 ± 81	470 ± 175
	Pond 1A	199 ± 153	233 ± 169	21 ± 48	453 ± 216
	Natural Wetlands	171 ± 138	5 ± 16	176 ± 195	352 ± 189
	Reference Wetlands	80 ± 75	25 ± 38	82 ± 45	187 ± 90
July 1994	Control	52 ± 60	41 ± 65	32 ± 47	125 ± 104
	Dyke Seepage	73 ± 53	14 ± 32	62 ± 111	147 ± 121
	Pond 1A	-	-	-	-
	Natural Wetlands	31 ± 40	5 ± 14	122 ± 101	157 ± 93
	Reference Wetlands	13 ± 21	4 ± 10	32 ± 28	30 ± 34
August 1994	Control	165 ± 145	42 ± 82	73 ± 93	271 ± 162
	Dyke Seepage	187 ± 116	62 ± 116	61 ± 94	306 ± 151
	Pond 1A	-	-	-	-
	Natural Wetlands	48 ± 69	7 ± 21	136 ± 96	191 ± 118
	Reference Wetlands	13 ± 22	7 ± 13	116 ± 72	122 ± 76
September 1994	Control	140 ± 157	41 ± 67	68 ± 131	249 ± 204
	Dyke Seepage	176 ± 158	42 ± 64	33 ± 76	251 ± 159
	Pond 1A	-	-	-	-
	Natural Wetlands	59 ± 61	2 ± 5	92 ± 143	153 ± 143
	Reference Wetlands	46 ± 62	8 ± 18	53 ± 78	105 ± 80

Table 4.4 Below-ground macrophyte biomass (mean ± standard deviation) in the constructed wetlands, 1993.

Treatment	Dry Weight ($g\ m^{-2}$)				Ratio Below:Above
	Typha latifolia	*Scirpus validus*	Total Below-ground	Total Above-ground	
Control	284±375	697±2413	981	518	1.9
Dyke Drainage	356±423	58±268	414	423	1.0
Pond 1A	306±411	500±945	806	432	1.9
Natural	206±179	0±0	206	176	1.2
Reference	84±161	12±39	96	105	0.9

Table 4.5 Decomposition (% reduction from initial mass, mean ± SD) of leaf litter over various exposure periods from 1992 - 1994.

Treatment	Exposure Period (days)						-k[b]	Half Life (d)[c]
	21	42[a]	63	84	290	438		
1992 (green *Typha latifolia*)								
Control	-	19±8	-	-	-	-	0.005	139
Dyke	-	19±30	-	-	-	-	0.005	139
Pond	-	9±9	-	-	-	-	0.002	347
1993 (green *Typha latifolia*)								
Control	44.7±4.0	52.2±9.1	48.3±6.4	-	61.8±26.6	66.7±22.6	0.018	39
Dyke	9.7±3.3	47.3±4.2	48.8±3.6	-	51.4±11.1	60±17.7	0.015	46
Pond	28.9±3.5	35.6±4.9	39.8±3.2	-	38.1±13.5	-	0.010	69
1994 (standing dead *Typha latifolia*)								
Control	14.5±3.4	18.9±6.2	-	23.3±8.9	-	-	0.005	139
Dyke	12.8±4.6	17.7±7.5	-	23.5±8.8	-	-	0.005	139
1994 (standing dead *Scirpus validus*)								
Control	17.4±3.4	24.3±7	-	32.8±12.9	-	-	0.007	99
Dyke	20.8±11.5	28.6±5.7	-	37.8±8.2	-	-	0.008	87

a actually only 41 day exposure period in 1992

b determined using data from 42 day exposure

$$\frac{Q_t}{Q_o} = e^{(-kt)}$$

where:

Q_0 = initial mass
Q_t = mass at time t
t = time, days
k = decay coefficient, day^{-1}

(Olson, 1963)

c calculated using decay coefficient determined from 42 day exposure

- no data

Table 4.6 Decay coefficients and half lives for litter under various water quality conditions.

Species	Water	Study Duration (d)	Decay Coefficient (k, day^{-1})	Half Life (days)	Reference
Typha spp.	Natural	30-60	0.0035-0.0018	197-395	Hershkowitz, 1986
		30 365	0.0154 0.0028	45 248	Thormann and Bayley, 1997
		180	0.0035	198	Boyd, 1970
		138	0.0240 (green) 0.0110 (senesced)	29 (green) 63 (senesced)	Nelson, 1990a
		300	0.0104	67	Webster and Simmons, 1978
		348	0.0019	365	Puriveth, 1980
	Waste-water	30-60	0.0074-0.0037	93-186	Kadlec, R.H., 1986
	Both	not given	0.0017	400±250	Kadlec R.H., 1986 and Kulshreshtha and Gopal, 1982
Scirpus spp.	Natural	not given	0.0027	260±80	Kulshreshtha and Gopal, 1982
Carex spp.	Natural	30-60	0.0011	610±320	Kadlec, R.H., 1986
		365	0.0002-0.0024 (green)	289-347	Thorman and Bayley, 1997
		365	0.0008-0.0016 (senescent)	433-866	Szumigalski and Bayley, 1996

assumes decomposition rate: $Q/Q_0 = e^{-kt}$

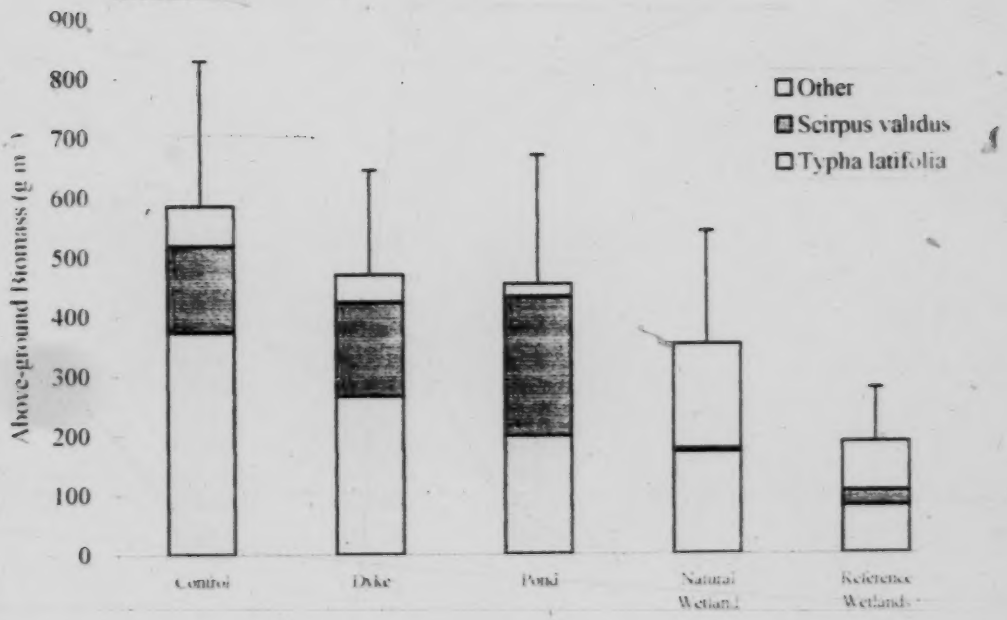

Figure 4.1 Above-ground macrophyte biomass (mean ± SD) in the constructed wetlands, September 1993.

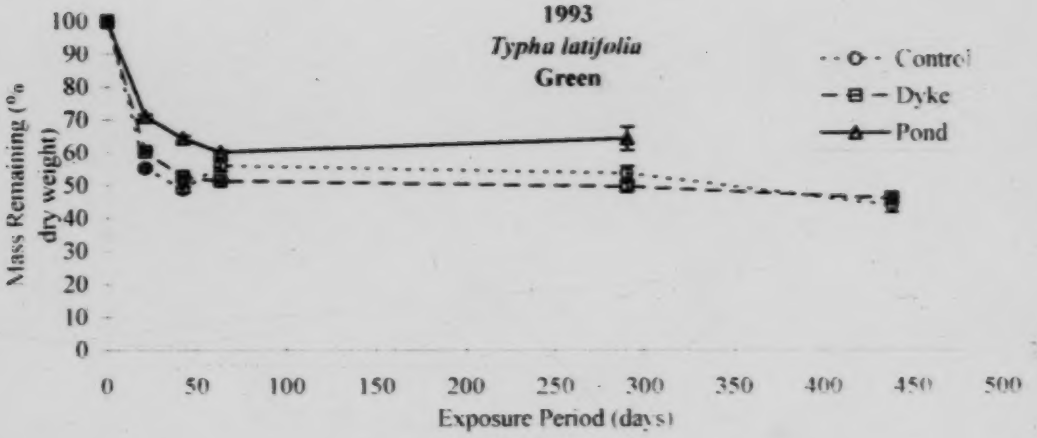

Figure 4.2 Mass remaining (dry weight as % of initial mass; mean ± SE) for *Typha latifolia* green leaves in 1993 in the constructed wetland trenches.

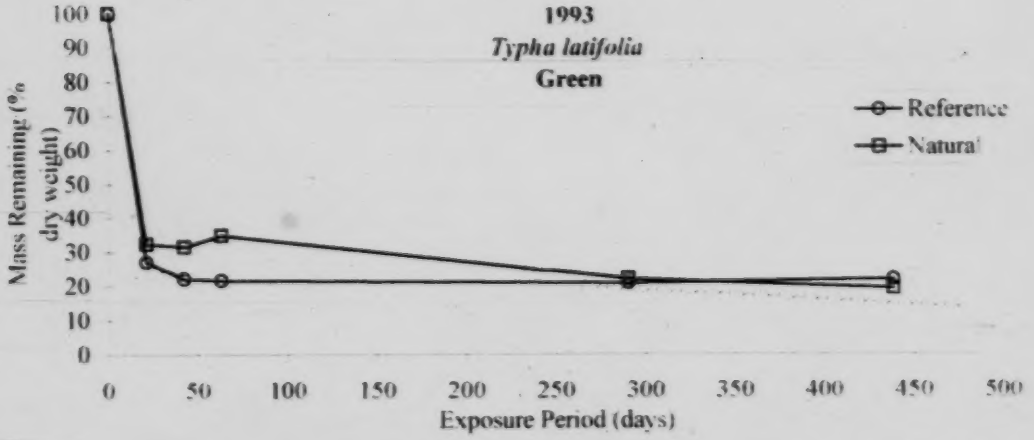

Figure 4.3 Mass remaining (dry weight as % of initial mass; mean ± SE) for *Typha latifolia* green leaves in 1993 in the Natural Wetland and Reference Wetlands.

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5.0 CONCLUSIONS

5.1 Scope of the problem

Suncor Inc., Oil Sands Group (Suncor) is the first of two companies mining oil sands in north eastern Alberta, 25 km north of Fort McMurray. The mining and subsequent conversion of oil sands to synthetic crude oil began in 1967. There are several environmental concerns associated with the production of synthetic crude oil. This study focused on the problem of the accumulating fine tailings.

In the process of extracting bitumen (*i.e.*, the Clark Hot Water Extraction Process) from the oil sands, a waste product called fine tailings is produced. Fine tailings are an aqueous suspension of sand, silt, clay and residual bitumen and naphtha with a pH between 8 and 9 (FTFC, 1995a). Fine tailings have been stored in large clay lined tailings ponds to date, which must be reclaimed to a viable land surface or water body free of long term maintenance (Nix and Martin, 1992).

There are two reclamation scenarios: dry landscape and wet landscape. There is a potential for water release from both dry and wet landscape scenarios. Although the water quality of these released waters is expected to be good (FTFC, 1995b), the contaminant load is unknown. To address this potential water release either a collection system must be maintained or a treatment system created. Wetlands could act as a polishing treatment system for water leaving the reclaimed site before entering the receiving environment. The potential for this was investigated in this study.

Organic (*e.g.*, naphthenic acids) and inorganic (*e.g.*, ammonia) contaminants are of concern in both waters tested (Dyke and Pond water). These contaminants (*i.e.*, naphthenic acid and ammonia) are of concern as they are toxic to aquatic organisms. The treatment effectiveness of wetlands to retain/remove ammonia and naphthenic acids (as measured by total extractable hydrocarbons or TEH) was assessed.

5.2 The potential for the use of wetlands to treat oil sands wastewater

The three previous Chapters addressed the potential for the use of wetland to treat oil sands wastewater by assessing treatment efficiency (Chapters

2 and 3) and wetland viability (Chapter 4). The potential of wetlands treatment was reviewed assessed in the proceeding chapters by addressing five issues below.

5.2.1 Do wetlands treat oil sands wastewater?

The contaminant concentrations were lower in the outflow water than inflowing water for Dyke and Pond water trenches. Both ammonia and TEH concentrations decreased from inflow to outflow.

Dyke inflow ammonia concentrations were in the range of 10 to 15 mg L^{-1}, and Pond inflow concentrations were in the range of 10 to 12 mg L^{-1}. Average Dyke outflow concentrations were in the range of 0.15 to 12 mg L^{-1}, and Pond outflow concentrations were in the range of 0.25 to 10 mg L^{-1}. Under comparable loading rates these outflow concentrations were comparable with the range of 0.2 mg L^{-1} to 48 mg L^{-1} reported in the literature (Hammer and Knight, 1994).

Dyke inflow TEH concentrations were in the range of 13 to 38 mg L^{-1}, and Pond inflow concentrations were in the range of 12 to 46 mg L^{-1}. Average Dyke outflow concentrations were in the range of 4 to 28 mg L^{-1}, and Pond outflow concentrations were in the range of 8 to 26 mg L^{-1}. These outflow concentrations were higher than the range of 0.1 mg L^{-1} to 2.0 mg L^{-1} reported in the literature for oil and grease (Table 3.3).

5.2.2 How well do wetlands treat this wastewater?

Although ammonia removal was substantial (ranging from 32 - 99 %) there was often still an order of magnitude difference between the Control trench outflows compared with either the Dyke or Pond trench outflows. In 1992 and 1994, removal rates were in the range of 44 % to 99 %; however, in 1993 removal rates were much lower (20 - 40 %) presumably because of the increased ammonia loading. At loading rates of 190 mg m^{-2} d^{-1} removal rates averaged > 90 %, while for higher loading rates of 270 mg m^{-2} d^{-1} removal rates averaged 75 %. Even lower removal efficiency (32 to 42 %) was observed for higher loading rates (605 to 785 mg m^{-2} d^{-1}), although similar loads were removed.

Ammonia was effectively removed by constructed wetlands receiving oil sands wastewater when compared with other treatment wetlands, despite

receiving a high load of hydrocarbons and being situated at a northern latitude. Observed data were comparable with predicted data using three ammonia removal models (Hammer and Knight, 1994; Reed et al., 1995; WPCF, 1990). Although observed values may have been statistically significantly different from the predicted values (12 of 15 data sets), ammonia removal was considered effective as the observed ammonia removal was often greater than the predicted removal (8 of 12 data sets).

Average TEH removal rates (*i.e.*, mass reductions) ranged from 19 % to 76 % for Dyke water and 54 % to 69 % for Pond water during the three year study. These rates were lower than rates for oil and grease reported in the literature (Table 3.3). The difference was probably due to the amount of contaminant loading. Contaminant loading was on average higher in this study ranging from 146 to 1143 mg m^{-2} d^{-1} compared with 32 to 168 mg m^{-2} d^{-1} for oil and grease removal in other studies.

5.2.3 Where do the contaminants go?

In 1994, the only year with a complete budget for ammonia nitrogen, the difference between inflow and outflow (*i.e.*, the amount of ammonia "retained" by the wetlands) was 4.8 kg $trench^{-1}$ $season^{-1}$ (206 mg m^{-2} d^{-1}), while the sum of the removal processes and change in nitrogen storage were only 2.35 kg $trench^{-1}$ $season^{-1}$ (or 101 mg m^{-2} d^{-1}). Plant storage did not contribute substantially to ammonia removal. Removal processes such as volatilization and denitrification, when measured in 1994, did not account for all the ammonia retained.

Ammonia removal to the sediments were 49 % (2.3 kg $trench^{-1}$ $season^{-1}$ or 101 mg m^{-2} d^{-1}) of the ammonia nitrogen retained (or perhaps more if immobilization occurred), while plant uptake accounted for approximately 2 % (0.10 kg $trench^{-1}$ $season^{-1}$; 4.5 mg m^{-2} d^{-1}). Nitrogen removal by plant uptake is not considered to be a main removal processes (van Oostrom and Russell, 1994; Richardson and Nichols, 1985; Klopateck, 1975 and 1978 cited in Richardson and Nichols, 1985; Gersberg, 1986).

Volatilization and denitrification accounted for approximately 0.1 % (0.004 kg $trench^{-1}$ $season^{-1}$ or 0.19 mg m^{-2} d^{-1}) and 4 % (0.19 kg $trench^{-1}$ $season^{-1}$ or 8.16 mg m^{-2} d^{-1}) of the ammonia retained, respectively. Volatilization of ammonia may account for losses up to 100 mg m^{-2} d^{-1} at pH 8 (based on an empirical equation developed for predicting ammonia volatilization from

flooded rice fields by Freney et al., 1985); however, using this study's data in the model 3.7 mg m^{-2} d^{-1} of ammonia could have been volatilized. Although denitrification is often assumed to be the primary removal process (Nichols, 1983), in this study it may only represent at most 50 % of the observed removal. However, denitrification (as measured) could not be verified experimentally to be the predominant pathway possibly due to the limitations of the technique rather than the lack of occurrence of denitrification (Seitzinger et al., 1993; Dalsgaard and Bak, 1992).

TEH removal to the sediments accounted for less than 30 % of the TEH load retained by the wetlands in this study. Other removal mechanisms include volatilization, plant uptake and microbial mineralization. Volatilization was not expected to be significant and parallel studies did not indicate plant uptake was significant and the removal via mineralization was unclear. Further method development is required to ensure processes and storage are reflected accurately.

Although some questions remain about the fate of both ammonia and TEH, removal was substantial. Further investigation to assess the role of constructed wetlands in the oil sands industry with respect to treatment and reclamation is warranted.

5.2.4 What factors affect wetland treatment efficiency of oil sands wastewater and can these factors be optimized?

Ammonia loading was observed to influence ammonia removal rates. Year 1 (1992) had a relatively low loading rate which resulted in a high treatment efficiency (*i.e.*, percent removal). Year 2 (1993) had a very high loading rate which resulted in a low treatment efficiency. Year 3 (1994) had an intermediate loading rate which resulted in an intermediate treatment efficiency. The same trend was observed for TEH removal. However, it may not just have been the ammonia and TEH loading rate responsible for the difference. Generally, with higher ammonia loading rates come higher TEH loading or visa versa, and for both lower dissolved oxygen. Higher TEH loading may lead to inhibition of nitrification or competition for resources from the hydrocarbon mineralizing microbes. Higher ammonia loading may lead to inhibition of TEH mineralization. Lower dissolved oxygen could limit nitrification. As ammonia is oxidized via nitrification approximately 4.6 g of oxygen is consumed per gram of ammonium nitrogen oxidized, which can deplete oxygen in the aquatic

environment (Reddy and Patrick, 1984). Lower dissolved oxygen could also limit hydrocarbon mineralization. The cause of decreased removal rates at higher loading was not determined.

5.2.5 Is treatment sustainable?

Although the potential impacts of oil sands wastewater (*i.e.*, Dyke and Pond water) on emergent aquatic macrophytes (hereafter referred to as macrophytes) are still not well understood, there is potential that both macrophyte production and decomposition may be negatively impacted by oil sands wastewater. As significant differences were only observed in 1993 (under higher loads), it is possible impacts can be controlled by controlling loading. Additionally, natural impacts such as the effect of muskrats or beavers may significantly affect the success of treatment constructed wetlands. A plan to address them should be included in the design, implementation and operation of treatment wetlands.

The most significant observation is that macrophytes continued to grow and appeared to "thrive" in the oil sands wastewaters after three "summers" of application. Given the high natural variability in production in wetlands, the effects of climate, muskrat activity and wastewater loading cannot be separated. Macrophyte production tended to be lower in trenches receiving oil sands wastewater, though not significantly. However, the sampling design may have been inadequate due to relatively high variation and a low number of replicates as suggested by the *a posteriori* power analysis. The lack of significant differences suggest no impact; however, the power of the study was low so the potential for accepting the null hypothesis when it was false was high. Larger-scale, longer-term demonstration wetlands are required before implementing treatment wetlands as part of mitigation design/mine closure.

Leaf litter provides surface area and nutrients for bacteria, and therefore can indirectly affect contaminant removal. In addition, decomposition plays an important role in overall wetland function by recycling nutrients. Although trends in decomposition were not statistically significant in all study years, there was some indication that oil sands wastewater could reduce litter decomposition. *A posteriori* power analysis indicated that there were insufficient replication at longer exposure periods, while at shorter exposure periods it was acceptable (*i.e.*, power of 80 %). Differences in decomposition under shorter exposure periods were only

detected under the higher loading in 1993. However, the cause of the observed decreased decomposition rates could have been the higher contaminant loads or low dissolved oxygen or some combination. The field studies did not determine cause.

The impact of reduced macrophyte production and/or decomposition rates on treatment efficiency and sustainability is unknown. In 1994, when the apparent production was substantially reduced by muskrats, wastewater treatment efficiency was not affected (Chapter 2). While no clear trend of contaminant impact on macrophyte production and/or decomposition was observed, it is important to note that loss of wetland function could limit the use of wetlands as a reclamation option and perhaps also as a treatment option for the oil sands industry.

5.3 Applicability to the Oil Sands Industry

The oil sands industry requires design criteria to implement treatment wetlands. To maintain removal rates of 70 % or more, the loading rates, should not exceed 270 mg m^{-2} d^{-1} and 210 mg m^{-2} d^{-1} for ammonia and TEH, respectively. Assuming the same water chemistry conditions as in 1994, the hydraulic loading rate should not exceed 1.8 cm/d or 0.6 cm/d to maintain ammonia and TEH removal, respectively. The estimated hydraulic loading rate for TEH removal is lower than for ammonia, and therefore could limit the design.

Alternatively, loadings could be reduced by some form of pre-treatment and/or removal rates could be enhanced to reduce land requirements. Although there are some indications that phosphate additions and increased oxygen (by alternating pond/wetland cells) enhance treatment (Bishay and Nix, 1996), further study would be required to develop design criteria. Should land availability not be an issue and treatment wetlands are the desired technology then sustainability must be ensured.

Under lighter loadings no differences in macrophyte production or decomposition were observed. However, at higher loadings macrophyte production and decomposition (of selected species) may be impacted. This suggests that a larger-scale, longer-term larger, demonstration project is needed to assess the sustainability of wetland treatment efficiency and of wetland function prior to the implementation of full-scale facilities.

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APPENDIX A

STUDY SITE DESCRIPTIONS

Appendix A.1 Contaminated Natural Wetlands and Constructed Wetlands

The study area, which includes the constructed wetlands and the contaminated wetland, is located southwest of Pond 2 between Dyke 2 and Highway 63. This area was disturbed during earlier mining, but was filled in with sand by 1984. A coke filter was installed along Dyke 2 in the fall of 1984 with collection lines to take seepage water to Extraction. A 15 cm layer of muskeg soil was spread over the area in 1985, initiating of reclamation procedures for the area. Surface water began pooling in the area, as the Dyke 2 west structure was being built, suggesting that the drainage system was not working effectively. The drainage lines were excavated and new lines installed along the toe of Dyke 2 in 1986-87. In the spring of 1988 the area was again disturbed by construction although reclamation had been completed on Dyke 2 west. Drainage ditches were constructed to remove some of the surplus water due to the high water table. Ditches (sloughs) were left in place with muskeg soil spread along their edges. The water in these ditches is a combination of local shallow groundwater, surface run-off and possibly tailings pond water seepage.

Since 1988 some of the surrounding areas have been colonized by emergent aquatic vegetation; consequently, prompting a feasibility study for the use of constructed wetland as a treatment "facility" for tailings pond water seepage. Water chemistry, toxicity and biological analyses were under taken in October of 1990 on the water flowing through the marsh to establish the extent of any "treatment" of the seepage water occurring. This marsh is now referred to as the "contaminated" wetland.

Although the study was composed of single samples taken on a single day trends from "upstream" to "downstream" were observed. Determining the causes of these trends was difficult due to the inability to separate the effect of dilution from the "treatment" process on the tailings pond water seepage in the study area; however, these results appeared promising and therefore Suncor decided to investigate the use of wetland for treatment of their waste water. Monitoring of this wetland continued in the 1992 field season with the data supporting this treatment of dyke seepage from inflow to outflow.

As a result of the field study in October 1990, Suncor began investigating the potential for wetlands to treat dyke seepage and Pond 1A top water. To investigate this treatment process a constructed wetland was built in the vicinity of the contaminated wetland.

The constructed wetlands were built in May and early June of 1991. The constructed wetland study area covers approximately 1.4 ha. There are nine trenches which are 50 m long and 2 m wide at the bottom. The trenches were planted with *Typha* sp. (cattail) and *Scripus* sp. (bulrush) in the week of June 10 to 14 and allowed to establish for the remainder of the 1991 growing season under ditch water conditions. There will be three treatments each having three replicate trenches: treatment 1 = control (ditch water), treatment 2 = dyke seepage water, treatment 3 = Pond 1A

tailings pond top water. Water from the three treatments began flowing June 29, 1992 at rate of ~ 2 L/min.

These trenches were fed from one of three tanks being supplied from the source (e.g., ditch - control , booster station - dyke seepage or Pond 1A top water) by either vacuum truck (for dyke seepage and Pond 1A top water) or pump through fire hose (for control water). Residence times in the tanks was approximately one week. This experimental facility will remain operational for at least 3 - 5 years.

Throughout the operation of these constructed wetland trenches various sampling programs will be implemented. The design for 1992 included chemical and toxicological analyses of the water from inflow, mid-trench and outflow, hydrological monitoring, and characterization of vegetation, phytoplankton, zooplankton, and benthic and microbial populations.

Appendix A.2 Reference Wetlands

All reference wetlands were not monitored in each study year due to logistical access problems, etc. A brief description of each wetland is provided below.

Shipyard Lake

Shipyard Lake is approximately 85 ha and is situated in the Athabasca River floodplain. This wetlands was monitored in 1992 only as access was difficult and because the wetlands quite different from the experimental wetlands. The southern portion of the wetlands can be classified as marsh while the northern portion is a mixture of swamp and marsh. The vegetation at the southern (upstream) end is dominated by *Typha latifolia* (cattail), *Phragmites australis* (reed) and *Acorus calanus* (sweetflag). The middle zone is characterized by *Equisetum fluviatile* (water horsetail), *P. australis*, and *T. latifolia*. The northern (downstream) end was characterized by swamp type vegetation including: tall shrubs (2-10 m) *Alnus tenuifolia* (river alder) and *Salix* spp. (willow), *Menyanthes trifoliata* (buckbeen), *T. latifolia*, *P. australis*, *Scirpus validus* (common great bulrush), *Scirpus microcarpus* (small fruited bulrush), *A. calanus*, *Sparaganium angustifolium* ssp. *emersum* (bur-reed), *Nuphar variegatum* (yellow pond-lily) and *Lemna*. Open water species include *Elodea canadensis* (Canada water weed) and *Myriophylum* sp. (water milfoil), *N. variegatum*, and *Lemna*.

Sediments had a silty-clay texture and had peat accumulations less than 50 cm in most areas.

Gravel Pit

This reference wetland was located approximately 15 m from a small road on land reclaimed from gravel pit operations. Although this wetland had a sandier substrate than the constructed wetlands it was selected as it was a reasonably young wetland and thought to be a better comparison than the well established Shipyard wetland. It was also a smaller wetland

(approximately 0.2 ha) again potentially a better comparison than the much larger Shipyard wetland. In addition, site access was much easier trip by road (i.e., <30 minute trip by road) than shipyard wetland was by boat and portage. This wetlands was used in 1993 and 1994.

AOSTRA Road

This reference wetland was located approximately 100 m from the gravel road to the AOSTRA facility. Although this wetland had a clayier substrate than the constructed wetlands it was selected as it was a reasonably young wetland and thought to be a better comparison than the well established Shipyard wetland. It was also a smaller wetland (approximately 0.2 ha) again potentially a better comparison than the much larger Shipyard wetland. In addition, site access was much easier trip by road (i.e., <30 minute trip by road) than shipyard wetland was by boat and portage. This wetlands was used in 1993 and 1994.

Highway 63

This reference wetlands covered approximately 2 ha and was located about 100 m from Highway #63 and about 2 km south of the Suncor Lease. It was monitored in 1994 only. This wetland was sought out in hopes of providing a reference wetlands with sediment more similar to the constructed wetlands compared with the Gravel Pit or AOSTRA road reference wetlands.

APPENDIX B

WATER CHEMISTRY METHODS AND QA/QC

Appendix B.1 - Laboratory Methods

University of Alberta Limnology Laboratory

Ammonia was determined from an unfiltered sample using the phenolhypochlorite method of Solórzano (1969) with the prepared samples being analyzed on the Technicon AutoAnalyzer. Nitrite-nitrate was determined from a filtered sample (0.45 µm HAWP Millipore filter) using the cadmium-copper reduction method of Stainton et al. (1977). TKN was determined using the sulphuric acid-copper sulphate method of D'Elia et al. (1977) and digested samples were analyzed using the Technicon AutoAnalyzer.

Suncor Laboratory

Ammonia was determined using an Orion Model EA 940 Expandable Ionanalyzer fitted with an ammonia selective electrode (Corning #476130) in accordance with the method 4500 - NH3 F outlined in APHA (1989). Nitrite-nitrate nitrogen was determined using Ion Chromatography (IC) using a carbonate biocarbonate element (1.7 mM) through a 4 mm packed polystyrene column. TKN was not analyzed at Suncor.

ASL Laboratory

Ammonia was determined colorimetrically using phenol and hypochlorite reagents in the presence of manganous salt in accordance with the method 4500 - NH3 - A, D and F as outlined in APHA (1989). Nitrite-nitrate was determined colorimetrically, after reduction with hydrazine sulphate, using sulphanilamide and N-1-naphthyl-ethylenediamine dihydrochloride reagents in accordance with the method 4500 - NO3 - A and H as outlined in APHA (1989). TKN was determined using a selective electrode after sulphuric acid, potassium sulphate and mercuric sulphate digestion in accordance with the method 4500 - N(org) - A and B as outlined in APHA (1989).

Appendix B.2 - QA/QC

As noted in Appendix B.1 three laboratories conducted the analyses. Most of the analyses were conducted by the University of Alberta; however, initially the other two labs were used. Comparisons were made between labs, although not for all sample periods, and the results are provided in Tables B.2-1, B.2-2 and B.2-3. The relative percent difference for ammonia within the three labs was 11%, 3% and 11% for the University of Alberta, Suncor and ASL. The RPD was 21% between ASL and Suncor and University of Alberta and Suncor.

Appendix B.2 Table B.2-1 QA/QC Summary.

Parameter	Comparison	Number of Comparisons	Relative Percent Difference		
			Minimum	Maximum	Median
Ammonia	within UA	21	3	61	11
	within Suncor	27	0	139	3
	within ASL	3	2	5	3
	between UA and Suncor	35	2	195	21
	between ASL and Suncor	48	0	181	21
Nitrite-Nitrate	within UA	2	6	116	61
	within Suncor	5	0	25	0
	within ASL	3	6	16	8
	between UA and Suncor	2	57	194	126
	between ASL and Suncor	48	1	187	133

Table B.2-2. Water chemistry results from ASL, Suncor and University of Alberta Labs, 1993

ASL Date	UA Date	Suncor Date	SITES	STN	SAMPLE	ASL - NH3	Sun-NH3	ASl-Sun	ASL-TKN	UA-TKN	ASL-NO2_NO3	Sun-NOx	ASl-Sun	ASL-NO2	ASL-NO3	ASL-TDP	ASL-T_P
4-Jul-93		4-Jul-93	T1	A	930020		0.1					0.1					
4-Jul-93		4-Jul-93	T1	D	930011	0.034	0.1	99	0.44		0.006	0.04	148	0.001	0.005		0.02
4-Jul-93		4-Jul-93	T148	A	930008	0.023	0.1	125	0.29		0.006	0.08	172	0.001	0.005		0.01
4-Jul-93		4-Jul-93	T2	A	930021		16.64					0.01					
4-Jul-93		4-Jul-93	T2	D	930012	10.8	10.64	1	8.73		0.036	0.05	33	0.021	0.015		0.005
4-Jul-93		4-Jul-93	T269	A	930009	16.5	19.2	15	12.8		0.006	0.03	133	0.001	0.005		0.022
4-Jul-93		4-Jul-93	T3	A	930022		12.32					0.06					
4-Jul-93		4-Jul-93	T3	D	930013	9.77	8.72	11	6.05		0.064	0.05	25	0.017	0.047		0.02
4-Jul-93		4-Jul-93	T357	A	930010	10.8	12.64	16	11.5		0.075	0.027	95	0.019	0.056		0.02
4-Jul-93		4-Jul-93	T4	A	930023		0.1					0.1					
4-Jul-93		4-Jul-93	T4	D	930014	0.028	0.1	113	0.35		0.006	0.01	50	0.001	0.005		0.021
4-Jul-93		4-Jul-93	T5	A	930024		11.92					0.01					
4-Jul-93		4-Jul-93	T5	D	930015	8.84	8.84	0	6.65		0.033	0.01	107	0.01	0.023		0.02
4-Jul-93		4-Jul-93	T6	A	930025		21.04					0.01					
4-Jul-93		4-Jul-93	T6	D	930016	10.1	10.28	2	7.69		0.079	0.05	45	0.017	0.062		0.008
4-Jul-93		4-Jul-93	T7	A	930026		13.68					0.01					
4-Jul-93		4-Jul-93	T7	D	930017	9.39	9.16	2	6.7		0.021	0.05	82	0.013	0.008		0.02
4-Jul-93		4-Jul-93	T8	A	930027		0.1					0.04					
4-Jul-93		4-Jul-93	T8	D	930018	0.044	0.1	78	0.47		0.006	0.08	172	0.001	0.005		0.025
4-Jul-93		4-Jul-93	T9	A	930028		19.92					0.07					
4-Jul-93		4-Jul-93	T9	D	930019	8.42	9.36	11	5.9		0.006	0.01	50	0.001	0.005		0.002
3-Aug-93	05-Aug-93	3-Aug-93	T1	A	930053		0.1			1.4546		0.15					
3-Aug-93	05-Aug-93	3-Aug-93	T1	D	930039	0.008	0.1	170	0.35	3.759	0.006	0.18	187	0.001	0.005		0.015
3-Aug-93	05-Aug-93	3-Aug-93	T148	A	930036	0.01	0.1	164	0.31		0.006	0.14	184	0.001	0.005		0.007
3-Aug-93	05-Aug-93	3-Aug-93	T2	A	930054		15.12			18.143		0.12					
3-Aug-93	05-Aug-93	3-Aug-93	T2	D	930040	10.9	11.64	7	10.3	21.446	0.069	0.15	74	0.021	0.048		0.008
3-Aug-93	05-Aug-93	3-Aug-93	T269	A	930037	14.8	14.84	0	15		0.023	0.123	137	0.014	0.009		0.005
3-Aug-93	05-Aug-93	3-Aug-93	T3	A	930055		15.24			39.78		0.13					
3-Aug-93	05-Aug-93	3-Aug-93	T3	D	930041	9.53	9.32	2	8.53	26.562	0.018	0.14	154	0.003	0.015		0.196
3-Aug-93	05-Aug-93	3-Aug-93	T357	A	930038	14.9	15.21	2	15.8		0.02	0.227	168	0.003	0.017		0.49
3-Aug-93	05-Aug-93	3-Aug-93	T4	A	930056		0.1			0.6109		0.1					
3-Aug-93	05-Aug-93	3-Aug-93	T4	D	930042	0.014	0.1	151	0.31	1.3313	0.006	0.1	177	0.001	0.005		0.013
3-Aug-93	05-Aug-93	3-Aug-93	T5	A	930057		15.36			12.384		0.41					

Table B.2-2. Water chemistry results from ASL, Suncor and University of Alberta Labs, 1993.

ASL Date	UA Date	Suncor Date	SITES	STN	SAMPLE	ASL - NH3	Sun-NH3	ASl-Sun	ASL-TKN	UA-TKN	ASL-NO2_NO3	Sun-NOx	ASl-Sun	ASL-NO2	ASL-NO3	ASL-TDP	ASL-T_P
3-Aug-93	05-Aug-93	3-Aug-93	T5	D	930043	10.1	10.04	1	9.25	17.905	0.054	0.24	127	0.003	0.051		0.231
3-Aug-93	05-Aug-93	3-Aug-93	T6	A	930058		14.48			15.965		0.13					
3-Aug-93	05-Aug-93	3-Aug-93	T6	D	930044	10.3	10.24	1	9.55	22.078	0.045	0.17	116	0.009	0.036		0.012
3-Aug-93	05-Aug-93	3-Aug-93	T7	A	930059		15.04			13.123		0.14					
3-Aug-93	05-Aug-93	3-Aug-93	T7	D	930045	10.8	10.56	2	12.2	11.184	0.047	0.16	109	0.002	0.045		0.206
3-Aug-93	05-Aug-93	3-Aug-93	T8	A	930060		0.1			0.37		0.17					
3-Aug-93	05-Aug-93	3-Aug-93	T8	D	930046	0.005	0.1	181	0.52	0.8046	0.006	0.17	186	0.001	0.005		0.016
3-Aug-93	05-Aug-93	3-Aug-93	T9	A	930061		14.92			16.275		0.12					
3-Aug-93	05-Aug-93	3-Aug-93	T9	D	930047	11	11.56	5	13.6	16.266	0.043	0.16	115	0.008	0.035		0.004
30-Aug-93		30-Aug-93	T1	A	930506		0.001					0.03					
30-Aug-93		30-Aug-93	T1	D	930484	0.007	0.001	150	0.29		0.006	0.001	143	0.001	0.005		0.014
30-Aug-93		30-Aug-93	T148	A	930481	0.011	0.001	167	0.3		0.008	0.011	29	0.003	0.005		0.007
30-Aug-93		30-Aug-93	T2	A	930507		16.08					0.12					
30-Aug-93		30-Aug-93	T2	D	930485	10.6	13.24	22	11.7		0.215	0.29	30	0.062	0.153		0.004
30-Aug-93		30-Aug-93	T269	A	930482	14	16	13	13.8		0.007	0.204	187	0.002	0.005		0.017
30-Aug-93		30-Aug-93	T3	A	930508		13.84					0.001					
30-Aug-93		30-Aug-93	T3	D	930486	10.2	11.76	14	8.84		0.007	0.001	150	0.002	0.005		0.103
30-Aug-93		30-Aug-93	T357	A	930483	11	14.05	24	10.3		0.011	0.001	167	0.005	0.006		0.069
30-Aug-93		30-Aug-93	T4	A	930509		0.001					0.001					
30-Aug-93		30-Aug-93	T4	D	930487	0.005	0.001	133	0.3		0.006	0.12	181	0.001	0.005		0.008
30-Aug-93		30-Aug-93	T5	A	930510		14.16					0.001					
30-Aug-93		30-Aug-93	T5	D	930488	8.22	10.76	27	8.47		0.01	0.001	164	0.005	0.005		0.081
30-Aug-93		30-Aug-93	T6	A	930511		16.28					0.49					
30-Aug-93		30-Aug-93	T6	D	930489	11.7	13.16	12	11.9		0.128	0.2	44	0.036	0.092		0.002
30-Aug-93		30-Aug-93	T7	A	930512		14.16					0.001					
30-Aug-93		30-Aug-93	T7	D	930490	10.1	12.68	23	9.4		0.007	0.001	150	0.002	0.005		0.177
30-Aug-93		30-Aug-93	T8	A	930513		0.001					0.001					
30-Aug-93		30-Aug-93	T8	D	930491	0.007	0.001	150	0.38		0.006	0.001	143	0.001	0.005		0.013
30-Aug-93		30-Aug-93	T9	A	930514		15.64					0.001					
30-Aug-93		30-Aug-93	T9	D	930492	11.2	13.56	19	10		0.227	0.31	31	0.056	0.171		0.004
27-Sep-93	20-Sep-93	27-Sep-93	T1	A	930574		0.01					0.1					
27-Sep-93	20-Sep-93	27-Sep-93	T1	D	930560	0.005	0.001	133	0.31		0.006	0.1	177	0.001	0.005		0.037
27-Sep-93	20-Sep-93	27-Sep-93	T148	A	930571	0.009	0.05	139	0.33		0.008	0.093	168	0.003	0.005		0.008

Table B.2-2. Water chemistry results from ASL, Suncor and University of Alberta Labs, 1993.

ASL Date	UA Date	Suncor Date	SITES	STN	SAMPLE	ASL - NH3	Sun-NH3	ASl-Sun	ASL-TKN	UA-TKN	ASL-NO2_NO3	Sun-NOx	ASl-Sun	ASL-NO2	ASL-NO3	ASL-TDP	ASL-T_P
27-Sep-93	20-Sep-93	27-Sep-93	T2	A	930575		18.82					0.12					
27-Sep-93	20-Sep-93	27-Sep-93	T2	D	930561	10.1	11.4	12	10.7		0.298	0.36	19	0.03	0.268		0.055
27-Sep-93	20-Sep-93	27-Sep-93	T269	A	930572	12.4	17.31	33	14.4		0.246	0.093	90	0.178	0.068		0.101
27-Sep-93	20-Sep-93	27-Sep-93	T3	A	930576		14.36					0.15					
27-Sep-93	20-Sep-93	27-Sep-93	T3	D	930562	8.78	12.8	37	12.1		0.046	0.09	65	0.021	0.025		0.275
27-Sep-93	20-Sep-93	27-Sep-93	T357	A	930573	12.3	11.54	6	12.4		0.016	0.13	156	0.01	0.006		0.51
27-Sep-93	20-Sep-93	27-Sep-93	T4	A	930577		0.08					0.09					
27-Sep-93	20-Sep-93	27-Sep-93	T4	D	930563	0.005	0.01	67	0.36		0.009	0.09	164	0.004	0.005		0.012
27-Sep-93	20-Sep-93	27-Sep-93	T5	A	930578		5.34					0.15					
27-Sep-93	20-Sep-93	27-Sep-93	T5	D	930564	4.04	4.92	20	6.76		0.052	0.13	86	0.015	0.037		0.585
27-Sep-93	20-Sep-93	27-Sep-93	T6	A	930579		16.72					0.09					
27-Sep-93	20-Sep-93	27-Sep-93	T6	D	930565	9.46	12.96	31	12		0.302	0.3	1	0.054	0.248		0.057
27-Sep-93	20-Sep-93	27-Sep-93	T7	A	930580		14.92					0.09					
27-Sep-93	20-Sep-93	27-Sep-93	T7	D	930566	10.1	11.72	15	13.8		0.02	0.1	133	0.011	0.009		0.39
27-Sep-93	20-Sep-93	27-Sep-93	T8	A	930581		0.06					0.09					
27-Sep-93	20-Sep-93	27-Sep-93	T8	D	930567	0.007	0.03	124	0.34		0.007	0.08	168	0.002	0.005		0.03
27-Sep-93	20-Sep-93	27-Sep-93	T9	A	930582		16.4					0.07					
27-Sep-93	20-Sep-93	27-Sep-93	T9	D	930568	9.9	12.56	24	10.9		0.376	0.41	9	0.041	0.335		0.03
n								48					48				
Min								0					1				
Max								181					187				
Median								21					133				

Table B 2-3. Water chemistry results from Suncor and University of Alberta Labs, 1994

Date	Treatment	Trench	Station	ID	Sun NHx	Sun Nox	S Var NH3	S Var NOx	UA NHx	UA NOx	Var UA NH	Var UA NO	lab NHx	lab NOx
12-Apr-94	NW	NW	In		7.1									
12-Apr-94	NW	NW	Mid		8.06									
12-Apr-94	NW	NW	Out		8.64									
12-Apr-94	NW	NW	Pipe		9.36									
12-Apr-94	Control	1	C		<0.1									
12-Apr-94	Dyke	2	C		1.75									
12-Apr-94	Dyke	3	C		1.23									
12-Apr-94	Control	4	C		<0.1									
12-Apr-94	Dyke	5	C		1.08									
12-Apr-94	Dyke	6	C		1.55									
12-Apr-94	Dyke	7	C		1.97									
12-Apr-94	Control	8	C		<0.1									
12-Apr-94	Dyke	9	C		0.606									
22-Apr-94	Dyke	oster Station			13.1									
25-Apr-94	Dyke	oster Station			15.8									
27-Apr-94	Dyke	oster Station			15.9									
28-Apr-94	Dyke	oster Station			18.1									
5-May-94	Dyke	oster Station			14.1									
30-May-94	Standard	6			5.19				6.1697				17	
30-May-94	NW	NW	Mid		3.88				4.8353				22	
30-May-94	Dyke	2	B	red	14.3		0							
30-May-94	Dyke	2	B	black	14.3									
30-May-94	Dyke	9	D	red					9.3491		2.733512			
30-May-94	Dyke	9	D	black					9.6082					
6-Jun-94	NW	NW	Mid		5.14		2.307692		4.9283		15.60504		4	
6-Jun-94	Dyke	NW	Mid	Y	5.26				4.2149				22	
6-Jun-94	Dyke	6	D		5.28		1.129944		6.5268		53.11655		21	
6-Jun-94	NW	6	D	X	5.34				3.7875				34	
6-Jun-94				Z					1.1759					
13-Jun-94	Dyke	9	D	AA	3.29		2.402402		3.5442		10.79689		7	
13-Jun-94	Dyke	9	D	BB	3.37				3.9487				16	
13-Jun-94	Control	8	D	DD	<0.1		0		<0.001					
13-Jun-94	Control	8	D	CC	<0.1				0.0107					
14-Jun-94	Standard	5		EE	5.39		7.8		5.2842		5.684		2	
14-Jun-94	Standard	1		FF	1.09		9		1.227		22.7		12	
14-Jun-94	Standard	0.1		JJ	<0.1		0		0.1086		8.6			
14-Jun-94	Standard	10		HH	10		0		9.3877		6.123		6	
14-Jun-94	Standard	18		II	21.3		18.33333		19.7065		9.480556		8	
14-Jun-94	Standard	6	ek old stan	GG	6.17		2.833333		4.982		16.96667		21	
21-Jun-94	Standard			CW-STD-OLD	4.43				5.421	0.2319			20	

Table B.2-3. Water chemistry results from Suncor and University of Alberta Labs, 1994.

Date	Treatment	Trench	Station	ID	Sun NHx	Sun Nox	S Var NH3	S Var NOx	UA NHx	UA NOx	Var UA NH	Var UA NO	lab NHx	lab NOx
21-Jun-94	Standard			CW-STD-X	5.16				6.7127	1.0645			26	
21-Jun-94	Standard			CW-STD-E	<0.1									
21-Jun-94	Standard			CW-STD-Y	1.19				1.6564				33	
21-Jun-94				CW-AA	4.31				5.5523	1.2609			25	
21-Jun-94				CW-CC	4.19									
28-Jun-94	Control	4	D		0.366		138.8889		0.0046				195	
28-Jun-94	Control	4	D		0.066				<0.001					
28-Jun-94	Dyke	6	D		2.188		1.102941		1.5832		11.41751		32	
28-Jun-94	Dyke	6	D		2.164				1.4122				42	
11-Jul-94	Dyke	9	D		3.56	<0.1	7.04607	0	3.2702	0.0097	39.00166	6.382979	8	
11-Jul-94	Dyke	9	D		3.82	<0.1			2.2029	0.0091			54	
11-Jul-94	Dyke	2	D		4.92	<0.1	4.179104	0	4.0061	0.0115		116.0584	20	
11-Jul-94	Dyke	2	D		5.13	<0.1				0.0433				
11-Jul-94	Standard	0.3		U52		0.3		0						
11-Jul-94	Standard	3		U55		2.25		25						
11-Jul-94	Standard	6		U56		5.47		8.833333						
11-Jul-94	Standard	0.2		AA	0.221	0.11	10.5		0.213	0.0612	6.5		4	57
11-Jul-94	Standard	4		BB	4.47		11.75		3.8053		4.8675		16	
11-Jul-94	Standard	8		CC	9.19	0.11	14.875		6.7933		15.08375		30	
18-Jul-94				NIT-CTRL-0		<0.1								
18-Jul-94				NIT-DYKE-02-0		<0.1								
18-Jul-94				NIT-DYKE-<0-0		<0.1								
18-Jul-94				NIT-DYKE-Cont	65.2									
18-Jul-94				NIT-Dyke-<0-0	22.6									
18-Jul-94				NIT-DYKE-02-0	24.2									
18-Jul-94	Standard	7.75		II	9		16.12903		4.9667		35.91355		58	
18-Jul-94	Standard	7.75		FF	7.8		0.645161		5.8399		24.64645		29	
18-Jul-94	Standard	0.4		GG	0.496		24		0.3781		5.475		27	
18-Jul-94	Standard	0.4		JJ	0.425		6.25		0.4114		2.85		3	
18-Jul-94	Dyke	2	D	373	4.88		0.61665		4.1829		18.63354		15	
18-Jul-94	Dyke	2	D		4.85				5.0424				4	
25-Jul-94	Dyke	6	D	1-237	3.86		1.56658		2.8644				30	
25-Jul-94	Dyke	6	D	357	3.8				2.8644				28	
25-Jul-94	Standard	9		AA	8.01		11		3.5118		60.98		78	
25-Jul-94	Standard	0.9		CL	0.879		2.333333							
25-Jul-94	Dyke	6	D	1-237		<0.1	0							
25-Jul-94	Dyke	6	D	357		<0.1								
25-Jul-94	Standard	0.13?		EE		<0.1								
25-Jul-94	Standard	1.8?		BB		0.704				0.0099				194
17-Aug-94	Dyke	2	A	N	15.6									

Table B 2-3. Water chemistry results from Suncor and University of Alberta Labs, 1994.

Date	Treatment	Trench	Station	ID	Sun NHx	Sun Nox	S Var NH3	S Var NOx	UA NHx	UA NOx	Var UA NH	Var UA NO	lab NHx	lab NOx
17-Aug-94	Dyke	2	A	V	17.1									
17-Aug-94	Dyke	6	A	N	13.7									
17-Aug-94	Dyke	6	A	V	13.1									
17-Aug-94	Dyke	9	A	N	13.6									
17-Aug-94	Dyke	9	A	V	13.8									
17-Aug-94	NW	In	In	N	11.2									
17-Aug-94	NW	In	In	V	11									
24-Aug-94				DS1	<0.1									
24-Aug-94				DS2	0.14									
24-Aug-94				DS3	<0.01									
24-Aug-94				DS4	0.018									
24-Aug-94				DS5	<0.1									
24-Aug-94				DS6	<0.1									
24-Aug-94				DS7	<0.1									
24-Aug-94				DS8	<0.1									
24-Aug-94				DS9	<0.1									
24-Aug-94				DS10	<0.1									
24-Aug-94				DS11	<0.1									
24-Aug-94				DS12	0.41									
24-Aug-94				DS13	<0.1									
24-Aug-94				DS14	0.34									
24-Aug-94				NST1	<0.1									
24-Aug-94				NST3	<0.1									
24-Aug-94				NST5	<0.1									
24-Aug-94				NST6	<0.1									
24-Aug-94				NST7	<0.1									
24-Aug-94				NST8	<0.1									
24-Aug-94				NST10	<0.1									
n							27	5			21	2	35	2
Min							0	0			3	6	2	57
Max							139	25			61	116	195	194
Median							3	0			11	61	21	126
Mean							11	7			18	61	28	126

APPENDIX C

HYDROMETEOROLOGY

C.1 Introduction

An understanding of the water balance or budget is paramount to determining contaminant fate/removal in treatment wetlands. That is, an accurate water mass balance is a prerequisite to an accurate contaminant mass balance (Kadlec and Knight, 1996). The mass balance must include: 1) a well defined system (i.e., a defined volume in space such as the surface water in a surface flow wetlands), 2) a time period over which inputs and outputs are totalled, 3) all inputs and outputs, 4) any reactions that produce or consume the chemical constituent of interest. The water mass balance was determined on a monthly basis for each study year, by measuring water flow in and out, precipitation and evapotranspiration. Groundwater inputs and outputs were assumed to be negligible since a plastic liner was installed in each trench.

C.2 Methods

Climate

The climate station installed in 1992 between the constructed wetlands and the natural wetlands was monitored on a daily basis. The station included a thermistor probe and a maximum/minimum thermometer in a standard Stephenson screen (air temperature), recording and non-recording rain gauges (rainfall depth and intensity), a 3-cup anemometer (wind run), and a Class A evaporation pan (evaporation). Signals from the thermistor probe and tipping bucket rain gauge were recorded automatically on data loggers (Lakewood R-X-6) at a scan interval of 10 minutes integrated every 60 minutes (except in 1994 when data was integrated every 6 hours). Manual collections were made from the evaporation pan and anemometer as well as a max/min thermometer. The time and frequency of manual collections varied, but generally occurred in the morning (generally between 0700 and 1000 h) at least 4 days a week. Recorded data were down loaded to a computer file at regular intervals. The climate station was fenced to prevent interference from animals.

Hydrology

Inflow and outflow rates were measured manually once or twice weekly at Stations A and D using a bucket and a stopwatch. Inflow rates were adjusted when necessary. Water levels were also measured at Station D continuously using Lakewood water level recorders which were placed in stilling wells adjacent to the weirs. Water level data were recorded with R-X-6 data loggers.

C.3 Results and Discussion

Climate

The monthly average temperature and precipitation data for the 1992-1994 monitoring periods (Atmospheric Environment Service, 1992, 1993, 1994) compared with normal temperature and precipitation (i.e., 30 year average data; Atmospheric Environment Service, 1993) for the Fort McMurray A

Climate Station are given in Table C.1. Mean daily temperatures from May to September were generally cooler in 1992 and 1993 than the 30 year average for Fort McMurray, while the opposite was observed for 1994. Total monthly precipitation in the same period was variable (i.e., no consistent trends between years for all months); however, precipitation in 1992 and 1993 was about the same as the 30 year average for Fort McMurray, while there was less precipitation in 1994. In general, 1994 was warmer and drier than average.

The monthly average temperature and precipitation data for 1992-1994 compared with study averages (i.e., 3 years from 1992 to 1994 inclusive) for on site climate station measurements are given in Table C.2. Average mean daily temperatures were cooler at Suncor than Fort McMurray except in September of 1992. The warmest mean daily temperatures (monthly average) were observed in July 1994 (manual 17.1°C; datalogger 17.7°C) and the coolest in September 1992 (datalogger 6.2°C)/September 1993 (manual 6.9°C). Extreme temperatures are provided in Table C.3a and 3b. The extreme minimum was observed in September 1992 (manual -9°C; datalogger -7.3°C) and the extreme maximum was observed in July 1994 (manual 34°C; datalogger - 34.8°C). Total monthly precipitation was about the same at Suncor site compared with Fort McMurray. On average 1992 may have been slightly wetter and 1993 and 1994 slightly drier. The highest monthly precipitation was observed in June 1992 (manual 119 mm; datalogger 115.2 mm) and the lowest in August 1994 (manual 15 mm; datalogger 20.4 mm).

In general, the manual and datalogger collections provided similar data. However, in water balance calculations the datalogger data was used only when a stage discharge relationship was derived. There is uncertainty or error associated with the measurement of precipitation: 1) misreading the scale (Winter, 1981); 2) failing to consider water (0.024 cm) required to moisten a dry gauge (Winter, 1981); 3) failing to consider the speed at which the tipping bucket tips during heavy rain which can result in underestimates of 5% (Linsely et al., 1958); 4) location of the gauge above the ground can result in underestimates of 5-15% at 1 m compared with ground level or higher if comparing for single storm event (Neff, 1977).

Another source of error occurs during aerial averaging of point data (i.e., each rain gauge) over the study area. For example, with a gauge density of 1 per 2,100 ha (21 km^2) or 1 per 240 ha (2.4 km^2) would result in an error of 11% or 4% respectively. However, this error is likely to be insignificant since the study area is relatively small (~3 to 3.5 ha which encompasses the climate station, contaminated natural wetlands, the constructed wetlands and surrounding area).

The tipping bucket data (i.e., the datalogger data) was chosen over the manually collected rain gauge data primarily because the gauge was not read every day during the study and as such would likely have the higher error. In general, one can assume approximately 1 to 5% instrument error, 5 to 15% placement error, up to 20% for lack of wind shield error, and < 4% averaging error (for a relatively small study area) (Winter, 1981). In this study our tipping bucket rain gauge was placed at ground level, therefore eliminating placement error. However, we did not have any wind

shields in place. The total possible error associated with the collection and use of the precipitation data could have been as high as 25%.

Evapotranspiration

Net (as measured) and total (corrected for precipitation) pan evaporation (from a Class 'A' Evaporation Pan at Suncor site) data are given in Table C.4. The monthly average evapotranspiration for 1992-94 compared with study averages (i.e., 3 years from 1992 to 1994 inclusive) for the on site weather station measurements and Complementary Relationship Areal Evapotranspiration (CRAE) at the Fort McMurray climate station (i.e., 17 year average data; Bothe and Abraham, 1987 and 1993) are given in Table C.5. Although evaporation pan coefficients have been shown to vary (Winter, 1981), a pan to wetlands coefficient of 0.8 was used to estimate wetlands evapotranspiration (Kadlec, 1989).

Evapotranspiration, as determined from pan evaporation, generally increased from 1992 to 1994 in any given month. Again indicating that 1994 was the driest year in the three year study. Although on average June tended to have the highest evapotranspiration, it was not the highest in all years. Evapotranspiration was lowest in September 1992 (23 mm) and highest in June 1994 (108 mm).

Hydraulic Retention Time

It is paramount to characterize the internal wetland water flows because studies of contaminant removal/nutrient cycling could otherwise be anomalous (Hammer and Kadlec, 1986). The design flow (i.e., the flow designated at the beginning of each study season) and therefore hydraulic retention time (HRT) varied between study years. The design flows were 2 L/min in 1992 and 1994 and 6 L/min in 1993. The nominal detention time can be calculated by dividing the volume of the trench by the input flow rate. The estimated volume of each trench is 52.5 m^3 (i.e., 50 m long x 3.5 m mean width x 0.35 m mean depth x an estimate of porosity, 0.9), and therefore the nominal detention time (or hydraulic retention time) for 2 L/min and 6 L/min flow was 19.1 days and 6.4 days, respectively; assuming approximate plug-flow conditions. Approximate plug-flow conditions do not generally occur in free-water surface wetlands, even in long narrow wetlands (Kadlec et al., 1993). Experimental verification of these estimated HRTs was required to accurately predict the range of contact times.

In 1993, hydrologic studies were conducted using bromide as a tracer to determine the HRT at 2, 6 and 20 L/min. The median HRTs were 17.1, 5.3 and 1.3 days, respectively (Nix et al., 1994). The median HRT represents the time it took 50% of the recovered bromide to pass through the constructed wetlands trench, while the 10% HRT and 90% HRT refer to the time it takes 10% and 90% of the bromide to pass through the trench. The 10% HRTs for 2 and 6 L/min flow were 10.8 and 3.6 days, respectively; while the 90% HRTs were 21 and 8.3 days, respectively (Nix et al., 1994). The median HRTs were actually very similar to the nominal HRTs; and therefore a 6 day HRT was assumed for the 6 L/min flow rates in all trenches.

In 1994, hydrologic studies included both bromide tracer and rhodamine dye tracers. These studies were only conducted in the split trenches as it was assumed that HRTs would not change from year to year assuming the flows tested were the same as those tested in 1993. The rhodamine dye was used primarily to assess tenplast berm integrity; while the bromide was used for HRT determinations and berm integrity. Based on flow, bromide tracer and rhodamine dye data, berm integrity was questionable for trench 3 (T3) and trench 5 (T5), therefore inflows and outflows were combined for the purposes of contaminant removal. Results for trench 7 (T7) berm were not as obvious; that is, some leakage was indicated by the rhodamine dye, but not the flow or bromide. However, the east and west sides were also combined for T7 for the purposes of the contaminant removal. The HRTs were 3 days for T3 (12 L/min), 24 days for T5 (1.5 L/min) and 17 days for T7 (2.25) or 9 days for T7W (2 L/min in half of trench) and 72 days for T7E (0.5 L/min in half of trench) (Nix et al., 1995). The HRTs for the remaining trenches was assumed to be 18 days at flow rate of 2 L/min based on the mean of 1993 tracer data and the nominal HRT.

Water Balance

Mean daily inflow measurements were made by stop watch and bucket. Mean daily discharge (i.e., outflow, L/min) was calculated by linear regression of instantaneous discharge measurements (by stop watch and bucket) on stage measurements (by float level indicator and datalogger) in addition to just means of manual discharge measurements.

Water balance estimates are valuable since they can be used to assess the role of precipitation and evapotranspiration on flow through the wetlands. Precipitation can increase flows and storage, while evapotranspiration may reduce flows and concentrate contaminants. Transpiration is the process where water is drawn from plant roots and transported to stomata in the leaves where the water is finally evaporated. Thus transpiration is the "engine" behind plant uptake processes. Evapotranspiration was estimated by the evaporation in a class 'A' pan monitored at the study site, and together with precipitation and flow data, water budgets for each trench were determined.

Flows for sampling days were extrapolated from flows around the sampling days. Average monthly flows are also given for each trench. Using monthly flows, precipitation and evaporation data the overall water budget for each trench was determined (Table C.6).

On average, unaccounted flow in 1992 was indicative of an unidentified input (i.e., 7% of the mean inflow of 1.52 L/min came from unmeasured inputs) while in 1993 and 1994 it was indicative of an unidentified output (16% of mean inflow of 5.65 L/min and 11% of mean inflow of 2.3 L/min, respectively left from unmeasured outputs). In all years the unaccounted portion of the inflow was less than 25% for all trenches except T1 in 1992 and 1994 and the split trenches (i.e., T3, T5 and T7) in 1994. The unaccounted flows that were less than 25% of the inflow were likely within the error of the measurement techniques and therefore it is unlikely that

the trenches leaked during the study period. Only T1 may have leaked, and since it was a Control trench it does not affect the nitrogen budget determined for wetlands receiving high ammonia loads. Therefore, no adjustments were made to trench flows and it was assumed that trenches were sealed from groundwater inputs/outputs.

A considerable proportion of the inflow water is not accounted for by the outflow, precipitation, evapotranspiration, which suggests that the trenches leak. However, the methods to derive estimates of flow, evapotranspiration, etc. are somewhat crude. For example, flow measurements were made with a bucket and stop watch and only during the day, thereby underestimating the actual outflow, because the outflow is expected to be higher at night when evapotranspiration is lower. Stage level was recorded using float level and datalogger; however, at this time stage flow relationships are not available for all years and therefore this data was not used.

The error associated with the various hydrometeorlogical parameters is as follows (Winter, 1981):

- precipitation measured with recording rain gauge - 2%
- evapotranspiration measured with Class A pan - 10%
- evaporation pan to lake/wetlands coefficient - 15%
- inflow with current meter - 5%
- outflow with current meter - 5%
- outflow stage discharge relationship - 5-10%

These errors may underestimate the actual error in the case of flow measurements since bucket and stopwatch measurements were made. They may also underestimate error associated with evapotranspiration since the pan to lake coefficient may have more error due to the small size of the wetlands which may result in increased evapotranspiration due to the oasis effect (Morton, 1983) and wicking. These errors would be the equivalent to the following on average from June to September inflow (units in L/min):

- total precipitation error of 2% --> 0.004 L/min
- total evapotranspiration error of 25% --> 0.07 L/min
- total inflow error of 5% --> 0.08 (for 1.52), 0.28 (for 5.65), 0.1 (for 2.33) L/min
- total outflow error of 15% --> 0.35 (for 2.33), 0.68 (for 4.5), 0.32 (for 2.15) L/min

Therefore, the total error could have been 0.5, 1, 0.5 L/min for 1992, 1993 and 1994, respectively. These errors are the equivalent to 33%, 18%, 21% of the inflow for 1992, 1993 and 1994, respectively. In 1992, the only trench where the unaccounted flow exceeded the measurement error of 33% was T1 (-72%), while all the rest were ≤ 15% of the inflow. In 1993, the unaccounted flow exceeded the measurement error of 18% in T1 (24%), T4 (20%), T5 (24%) and T8 (21%). In 1994, the unaccounted flow exceed the measurement error of 21% in T1 (35%) and the three split trenches (-40%, -40% and -29% for T3, T5, T7, respectively). Essentially, T1 outputs were overestimated or inputs underestimated in 1992 which is not indicative of a leak; however, in 1993 and 1994 the reverse was true therefore indicating

a leakage may have occurred. Although there were other trenches where the unaccounted flow exceeded the estimated error, these values were very close and therefore no other trench's integrity was questioned except for the split trenches in 1994. The integrity of T1 does not affect the determination of the nitrogen budget as it was Control trench.

Table C.1 Average temperatures and precipitation rates at the Fort McMurray A Climate Station for 1992-1994 compared with 30 year averages.

Month	Mean Daily Temperature (°C)				Total Monthly Precipitation (mm)			
	1992	1993	1994	Normal (1961-1990)	1992	1993	1994	Normal (1961-1990)
May	9.2	na	11.2	10.1	20.8	na	22.8	40.7
June	14.1	13.4	15.2	14.6	108.2	72.8	61.0	63.9
July	15.7	15.3	17.8	16.6	39.6	78.6	94.6	79.1
August	14	14.5	16.3	15.2	52.4	50.1	7.4	71.8
September	6.7	8.6	12.0	9.1	69.0	34.4	19.0	51.4

na not available

Table C.2a Average temperatures and precipitation rates at the Suncor Climate Station for 1992-1994 compared with 1992-1994 averages: Manual.

Month	Mean Daily Temperature (°C)				Total Monthly Precipitation (mm)			
	1992	1993	1994	(1992-94)	1992	1993	1994	(1992-94)
May	-	11.3	10.4	10.9	-	47	20	33
June	12.9	12.3	14.4	13.2	119	67	86	91
July	14.5	13.4	17.1	15.0	40	81	57	59
August	13.2	13.1	15.9	14.1	42	29	15	29
September	7.4	6.9	11.0	8.4	55	33	36	41

- incomplete data set

Table C.2b Average temperatures and precipitation rates at the Suncor Climate Station for 1992-1994 compared with 1992-1994 averages: Datalogger.

Month	Mean Daily Temperature (°C)				Total Monthly Precipitation (mm)			
	1992	1993	1994	(1992-94)	1992	1993	1994	(1992-94)
May	-	10.9	11.5	11.2	-	48.4	19.4	33.9
June	12.5	13.4	14.9	13.6	115.2	72.6	87.8	91.9
July	15.6	15.4	17.7	16.2	28.4	50.4	60.4	46.4
August	12.9	14.2	16.0	14.4	48.6	30.0	20.4	33
September	6.2	8.2	11.2	8.5	80.6	31.8	38.0	50.1

Table C.3a Minimum and maximum daily temperatures at the Suncor Climate Station for 1992-1994 compared with 1992-1994 averages: Manual.

Month	Minimum Daily Temperature (°C)				Maximum daily Temperature (°C)			
	1992	1993	1994	(1992-94)	1992	1993	1994	(1992-94)
May	-	-6	-6	-6	-	30	28	29
June	-1	-7	-2	-3	31	29	30	30
July	1	2	4	2	30	27	34	30
August	-5	-3	-2	-3	33	30	30	31
September	-9	-8	-3	-7	21	29	27	26

Table C.3b Minimum and maximum daily temperatures at the Suncor Climate Station 1992-1994 compared with 1992-1994 averages: Datalogger.

Month	Minimum Daily Temperature (°C)				Maximum daily Temperature (°C)			
	1992	1993	1994	(1992-94)	1992	1993	1994	(1992-94)
May	-	-4.6	-5.7	-5.2	-	30.7	28.5	29.6
June	-	-2.5	-1.5	-2.0	-	29.2	31.3	30.3
July	1.3	4.8	3.7	3.3	27.8	26.6	34.8	29.7
August	-3.8	-1.1	-1.7	-2.2	32.8	30.3	30.4	31.2
September	-7.3	-6.0	-3.9	-5.7	26.4	25.3	28.6	26.8

Table C.4 Net and Total Evaporation (using a Class 'A' Evaporation Pan) at the Suncor Wetlands Study site.

Month	Monthly Net Evaporation[a] (mm)			Monthly Total Evaporation[b] (mm)		
	1992	1993	1994	1992	1993	1994
May	-	80.4	80.3	-	84.2	100.9
June	16.7	55	49.6	66.3	121.6	134.5
July	52.1	13.6	50.8	91.8	93.3	108.1
August	33.8	54.8	85.7	75.8	83.6	100.7
September	-26.1	65.4	14.4	29.2	37.4	50.3

a - net evaporation was the change measured in the evaporation pan
b - total evaporation equals net evaporation + precipitation

Table C.5 Evapotranspiration at the Suncor Wetlands Study site for 1992-1994 compared with 17 year averages at Fort McMurray, AB.

Month	Evapotranspiration[a] (mm)				
	Monthly			Three (1992-94) year	Normal (1972-1992)
	1992	1993	1994		
May	-	67	81	74	39
June	53	97	108	86	66
July	73	75	86	78	80
August	61	67	81	70	54
September	23	30	40	31	16

a 80% of total evaporation is generally accepted to equal evapotranspiration in a wetlands (Kadlec and Knight, 1996)

NOTE TO USERS

Page(s) not included in the original manuscript are unavailable from the author or university. The manuscript was microfilmed as received.

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APPENDIX D

TREATMENT EFFICIENCY COMPARISON WITH THREE MODELS

Appendix D.1 Model Descriptions

Model 1 assumes that constructed wetlands are attached growth biological reactors and that their performance can be estimated by first-order plug-flow kinetics (Reed et al., 1995). The basic equation is as follows:

$$C_e = \frac{C_o}{e^{(\frac{A_s k_t y n}{Q})}}$$

OR

$$C_e = \frac{C_o}{e^{(\frac{HRT k_t}{Q})}}$$

Where:

C_0 = initial/inflow ammonia concentration (mg N/L)
C_e = effluent/outflow ammonia concentration (mg N/L)
A_s = wetland area (m^2)
k_t = temperature dependent first order reaction rate constant, $days^{-1}$

For:		
	0°C	$k_t = 0\ (d^{-1})$
	1- 10°C	$k_t = 0.1367 * 1.15^{(T-10°)}\ (d^{-1})$
	>10°C	$k_t = 0.2187 * 1.048^{(T-20°)}\ (d^{-1})$

y = mean water depth (m)
n = porosity or space available for water to flow through the wetland
Q = flow (m^3/d)
HRT = hydraulic retention time (d)

Model 2 is based on a regression analysis of data from constructed and natural wetland treatment systems (WPCF, 1990). The basic equation is as follows:

$$\ln C_e = 0.688 \ln C_0 + 0.655 \ln HLR - 1.107$$

Where:

C_0 = initial/inflow ammonia concentration (mg N/L)
C_e = effluent/outflow ammonia concentration (mg N/L)
HLR = hydraulic loading rate (cm/d)
i.e., flow (m^3/d) * area (m^2) * 100

Model 3 is based on a regression analysis of data from 17 free surface constructed wetland treatment systems (Hammer and Knight, 1994). The basic equation is as follows:

$$C_e = -0.161 + 1.83\ L_0$$

Where:

L_0 = ammonia loading (kg N/ha/day)
i.e., $C_0/1000*Q/A/100$
C_0 = initial/inflow ammonia concentration (mg N/L)
Q = flow (m^3/d)
A = wetland area (m^2)
C_e = effluent/outflow ammonia concentration (mg N/L)

References Cited

Hammer, D.A. and R.L. Knight. 1994. Designing constructed wetlands for nitrogen removal. *Water Science and Technology.* 29(4):15-27.

Reed, S.C., R.W. Crites and E.J. Middlebrooks. 1995. *Natural systems for waste management and treatment.* McGraw-Hill Inc., New York.

Water Pollution Control Federation (WPCF). 1990. Natural systems for wastewater treatment. MOP FD-16. Imperial Printing, St. Joseph, Michigan.

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
2	T2	A	1-Jul-92	18	0.0079	2	0.02	20.2	0.00027	1.797	0.00	21.4	0.2271	0.00	1.6457	0.02	2.88	-0.16
2	T6	A	1-Jul-92	18	0.0079	2	0.02	22.7	0.00031	1.797	0.00	21.4	0.2408	0.00	1.6457	0.02	2.88	-0.16
2	T9	A	1-Jul-92	18	0.0079	2	0.02	21.45	9.1E-05	1.797	0.00	21.4	0.2338	0.00	1.6457	0.02	2.88	-0.16
2	T2	A	16-Jul-92	18	0.0133	0.286	0.00	17.4	0.00012	0.167	0.00	16	0.1874	0.00	0.2353	0.01	0.41	-0.16
2	T6	A	16-Jul-92	18	0.0133	2.143	0.03	17.7	0.00011	0.167	0.00	16.5	0.1909	0.00	1.7634	0.02	3.09	-0.16
2	T9	A	16-Jul-92	18	0.0133	2	0.03	17.8	4.5E-05	1.875	0.00	16.7	0.1922	0.00	1.6457	0.02	2.88	-0.16
2	T2	A	20-Jul-92	18		1.429		18.3		0.167		18.3						
2	T6	A	20-Jul-92	18		1.364		18.4		0.2		19.1						
2	T9	A	20-Jul-92	18		1.429		18.5		0.682		21						
2	T2	A	22-Jul-92	18		3.333		18.6		3		17.3						
2	T6	A	22-Jul-92	18		2.727		19.4		1.765		18.1						
2	T9	A	22-Jul-92	18		3		19.4		4.286		18.7						
2	T2	A	1-Aug-92	18	0.0137	1.902	0.03	18.5	0.00054	1.56	0.00	19.9	0.2106	0.00	1.5651	0.02	2.74	-0.16
2	T6	A	1-Aug-92	18	0.0137	2.625	0.04	18.9	1.2E-05	1.636	0.00	19.7	0.2116	0.00	2.1600	0.03	3.78	-0.16
2	T9	A	1-Aug-92	18	0.0137	2.527	0.03	18.8	9.8E-05	2.121	0.00	19.6	0.2106	0.00	2.0794	0.03	3.64	-0.16
2	T2	A	17-Aug-92	18		1.304		18.9		0.811		13.2						
2	T6	A	17-Aug-92	18		2.625		19.2		1.636		13.5						
2	T9	A	17-Aug-92	18		2.527		19		2.595		13.7						
2	T2	A	23-Aug-92	18		1.875		11.8		1.765		11.1						
2	T6	A	23-Aug-92	18		2		13		1.579		12.1						
2	T9	A	23-Aug-92	18		1.364		13.6		2		13.5						
2	T2	A	2-Sep-92	18		1.667		13.2		1.765		13.4						
2	T6	A	2-Sep-92	18		1.765		13.6		1.5		13.5						
2	T9	A	2-Sep-92	18		1.875		13.6		1.5		14.2						
2	T2	A	3-Sep-92	18		1.765		10.3		1.667		9						
2	T6	A	3-Sep-92	18		1.765		11.2		1.111		9.5						
2	T9	A	3-Sep-92	18		1.875		11.9		1.579		9.7						
2	T2	A	8-Sep-92	18		1.429		9.8		5		7.8						
2	T6	A	8-Sep-92	18		1.579		10.3		3		7.7						
2	T9	A	8-Sep-92	18		1.25		10.7		3		7.8						
2	T2	A	10-Sep-92	18		2		15.3		2.308		13						
2	T6	A	10-Sep-92	18		2.308		14.1		1.364		12.1						
2	T9	A	10-Sep-92	18		1.667		13.3		1.5		13						
2	T2	A	26-Sep-92	18		1.579		4.3		2		5.9						
2	T6	A	26-Sep-92	18		2		4.9		2		5.8						
2	T9	A	26-Sep-92	18		1.875		5.2		2		5.7						
			Min		0.0079	0.286	0.0038	4.3	1.2E-05	0.167	1.9E-05	5.7	0.1874	0.00	0.2353	0.01	0.41	-0.16
			Median		0.0133	1.875	0.02606	16.35	0.00011	1.765	0.00016	13.5	0.2106	0.00	1.6457	0.02	2.88	-0.16
			Max		0.0137	3.333	0.03596	22.7	0.00054	5	0.00084	21.4	0.2408	0.00	2.1600	0.03	3.78	-0.16

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters								
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
			Mean		**0.01163**	**1.91275**	**0.02255**	**15.0902778**	**0.00018**	**1.797139**	**0.00027**	**14.175**	**0.2117**	**0.00**	**1.5984**	**0.02**	**2.80**	**-0.16**
			SD		**0.00281**	**0.562374**	**0.01048**	**4.71807799**	**0.00017**	**1.012099**	**0.00029**	**4.85276799**	**0.0193**	**0.00**	**0.5525**	**0.01**	**0.97**	**0.00**
			n		**9**	**36**	**9**	**36**	**9**	**36**	**9**	**36**	**9.0000**	**9.00**	**9.0000**	**9.00**	**9.00**	**9.00**
2	T2	A	21-Jun-93	6		6.25		16.2		4.53		14.2						
2	T6	A	21-Jun-93	6		6.25		16.4		5.34		14.4						
2	T9	A	21-Jun-93	6		2.125		16.3		2.965		15.2						
2	T2	A	28-Jun-93	6	0.01882	6.5	0.12	15.3	0.01368	5	0.07	14.5	0.1722	0.01	5.3486	0.06	9.36	-0.14
2	T6	A	28-Jun-93	6	0.01852	6	0.11	15	0.01184	6	0.07	14.1	0.1694	0.01	4.9371	0.06	8.64	-0.14
2	T9	A	28-Jun-93	6	0.01944	2	0.04	15	0.0036	4.5	0.02	14.4	0.1706	0.01	1.6457	0.03	2.88	-0.15
2	T2	A	4-Jul-93	6	0.017	5.875	0.10	17.5	0.0092	4.475	0.04	20.1	0.2067	0.00	4.8343	0.06	8.46	-0.15
2	T6	A	4-Jul-93	6	0.01628	5.75	0.09	17.5	0.0112	3.105	0.03	20.5	0.2087	0.00	4.7314	0.05	8.28	-0.15
2	T9	A	4-Jul-93	6	0.01992	4.25	0.08	17.2	0.01256	2	0.03	20.5	0.2072	0.01	3.4971	0.05	6.12	-0.15
2	T2	A	9-Jul-93	6		5.875		15		4.475		14.3						
2	T6	A	9-Jul-93	6		5.75		15.3		3.105		13.2						
2	T9	A	9-Jul-93	6		4.25		15.3		2		12.6						
2	T2	A	13-Jul-93	6	0.01512	5.625	0.09	15.8	0.0133	3.875	0.05	14.1	0.1726	0.01	4.6286	0.05	8.10	-0.15
2	T6	A	13-Jul-93	6	0.01448	6	0.09	15.8	0.01028	4.75	0.05	16.4	0.1822	0.00	4.9371	0.05	8.64	-0.15
2	T9	A	13-Jul-93	6	0.01528	5.875	0.09	15.4	0.01136	4.5	0.05	16.3	0.1800	0.01	4.8343	0.05	8.46	-0.15
2	T2	A	19-Jul-93	6	0.0144	6	0.09	17.7	0.01104	5.75	0.06	15.4	0.1860	0.00	4.9371	0.05	8.64	-0.15
2	T6	A	19-Jul-93	6	0.01616	6	0.10	18.3	0.01328	5	0.07	16.6	0.1941	0.01	4.9371	0.06	8.64	-0.15
2	T9	A	19-Jul-93	6	0.01564	6	0.09	18	0.0122	5	0.06	17.1	0.1950	0.00	4.9371	0.05	8.64	-0.15
2	T2	A	27-Jul-93	6	0.01516	6	0.09	19.6	0.01064	6.127	0.07	16.7	0.2005	0.00	4.9371	0.05	8.64	-0.15
2	T6	A	27-Jul-93	6	0.01416	6.5	0.09	20	0.01024	3.25	0.03	18.8	0.2126	0.00	5.3486	0.05	9.36	-0.15
2	T9	A	27-Jul-93	6	0.01628	6.25	0.10	19.5	0.01156	6.5	0.08	19.8	0.2151	0.00	5.1429	0.06	9.00	-0.15
2	T2	A	3-Aug-93	6	0.0176	6	0.11	17.5	0.01256	4.337	0.05	19.7	0.2048	0.01	4.9371	0.06	8.64	-0.14
2	T6	A	3-Aug-93	6	0.01488	6.25	0.09	17.5	0.01356	3.625	0.05	18.6	0.1996	0.00	5.1429	0.05	9.00	-0.15
2	T9	A	3-Aug-93	6	0.0166	6.5	0.11	17.3	0.01204	5.5	0.07	17.9	0.1954	0.01	5.3486	0.06	9.36	-0.14
2	T2	A	9-Aug-93	6	0.01812	6	0.11	17.8	0.01324	5.5	0.07	15.3	0.1860	0.01	4.9371	0.06	8.64	-0.14
2	T6	A	9-Aug-93	6	0.016	7	0.11	17.8	0.01316	5	0.07	15.6	0.1874	0.01	5.7600	0.06	10.08	-0.14
2	T9	A	9-Aug-93	6	0.01528	8.5	0.13	17.5	0.0136	8	0.11	15.3	0.1847	0.01	6.9943	0.07	12.24	-0.14
2	T2	A	16-Aug-93	6	0.0154	6	0.09	17.3	0.011	5	0.06	17.4	0.1931	0.00	4.9371	0.05	8.64	-0.15
2	T6	A	16-Aug-93	6	0.0196	6	0.12	16.5	0.01296	4.25	0.06	15.6	0.1817	0.01	4.9371	0.06	8.64	-0.14
2	T9	A	16-Aug-93	6	0.0164	6	0.10	15.9	0.011	5	0.06	13.3	0.1698	0.01	4.9371	0.06	8.64	-0.15
2	T2	A	23-Aug-93	6	0.0156	6	0.09	19.8	0.012	6.625	0.08	16.7	0.2015	0.00	4.9371	0.05	8.64	-0.15
2	T6	A	23-Aug-93	6	0.01628	6	0.10	19.2	0.01168	5.625	0.07	15.8	0.1945	0.01	4.9371	0.06	8.64	-0.15
2	T9	A	23-Aug-93	6	0.01492	6	0.09	18.6	0.01356	5.125	0.07	14.1	0.1843	0.00	4.9371	0.05	8.64	-0.15
2	T2	A	30-Aug-93	6	0.01608	6	0.10	15.1	0.0114	5.625	0.06	12.6	0.1639	0.01	4.9371	0.05	8.64	-0.15
2	T6	A	30-Aug-93	6	0.01672	6	0.10	15.1	0.01088	5.625	0.06	11.7	0.1605	0.01	4.9371	0.06	8.64	-0.15
2	T9	A	30-Aug-93	6	0.0178	6.125	0.11	14.6	0.01672	5.625	0.09	10.7	0.1550	0.01	5.0400	0.06	8.82	-0.14

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
2	T2	A	7-Sep-93	6	0.01432	6	0.09	14.1	0.01204	6	0.07	10.9	0.1539	0.01	4.9371	0.05	8.64	-0.15
2	T6	A	7-Sep-93	6	0.01708	6	0.10	13.6	0.01148	5.625	0.06	10.2	0.1496	0.01	4.9371	0.06	8.64	-0.15
2	T9	A	7-Sep-93	6	0.01584	6.125	0.10	14.1	0.01144	5.625	0.06	9.5	0.1489	0.01	5.0400	0.06	8.82	-0.15
2	T2	A	13-Sep-93	6	0.01664		0.00	11.7	0.01164		0.00	6.9	0.1240	0.01	0.0000		0.00	
2	T6	A	13-Sep-93	6	0.02104	6	0.13	11.3	0.00928		0.00	6	0.1132	0.01	4.9371	0.07	8.64	-0.14
2	T9	A	13-Sep-93	6	0.01708	6.25	0.11	11	0.01256		0.00	4.5	0.0998	0.01	5.1429	0.06	9.00	-0.14
2	T2	A	20-Sep-93	6	0.0178			12	0.01284			8	0.1367	0.01	0.0000		0.00	
2	T6	A	20-Sep-93	6	0.00064			11.7	0.01324			7.6	0.1302	0.00	0.0000		0.00	
2	T9	A	20-Sep-93	6	0.02452			11.5	0.01516			6.2	0.1164	0.01	0.0000		0.00	
2	T2	A	27-Sep-93	6	0.01368			8.9	0.009			6.8	0.1012	0.01	0.0000		0.00	
2	T6	A	27-Sep-93	6	0.01596			8.4	0.0124			6.6	0.0964	0.01	0.0000		0.00	
2	T9	A	27-Sep-93	6	0.0134			8.4	0.00936			5.4	0.0886	0.01	0.0000		0.00	
2	T2	A	4-Oct-93	6				4.2				4.4						
2	T6	A	4-Oct-93	6				4				4.8						
2	T9	A	4-Oct-93	6				4.1				4.8						
2	T2	A	12-Oct-93	6				1.2				4.9						
2	T6	A	12-Oct-93	6				1.7				4.7						
2	T9	A	12-Oct-93	6				1.2				5.6						
			Min		**0.00064**	**2**	**0**	**1.2**	**0.0036**	**2**	**0**	**4.4**	**0.0886**	**0.00**	**0.0000**	**0.03**	**0.00**	**-0.15**
			Median		**0.01622**	**6**	**0.09699**	**15.35**	**0.01192**	**5**	**0.06234**	**14.15**	**0.1809**	**0.01**	**4.9371**	**0.06**	**8.64**	**-0.15**
			Max		**0.02452**	**8.5**	**0.12988**	**20**	**0.01672**	**8**	**0.1088**	**20.5**	**0.2151**	**0.01**	**6.9943**	**0.07**	**12.24**	**-0.14**
			Mean		**0.01624**	**5.85061**	**0.09569**	**14.1240741**	**0.0118**	**4.870744**	**0.05529**	**12.7277778**	**0.1689**	**0.01**	**4.1020**	**0.06**	**7.18**	**-0.15**
			SD		**0.00325**	**1.059267**	**0.02247**	**4.93932755**	**0.00202**	**1.234647**	**0.0241**	**4.98890908**	**0.0352**	**0.00**	**1.9753**	**0.01**	**3.46**	**0.00**
			n		**42**	**41**	**36**	**54**	**42**	**39**	**36**	**54**	**42.0000**	**42.00**	**42.0000**	**35.00**	**42.00**	**35.00**
2	T2	A	30-May-94	18	17.4773	5.438	95.04		10.8646	4.76	51.72	13	0.1575	1.03	4.4747	6.31	7.83	14.16
2	T6	A	30-May-94	18	17.4876	6.103	106.73		8.2994	0	0.00	13	0.1575	1.03	5.0219	6.81	8.79	15.92
2	T9	A	30-May-94	18	16.228	6.144	99.70		9.3491	5.347	49.99	13	0.1575	0.95	5.0556	6.50	8.85	14.86
2	T2	A	6-Jun-94	18	16.1714	3.234	52.30	21	8.8689	2	17.74	21	0.2292	0.26	2.6611	4.26	4.66	7.72
2	T6	A	6-Jun-94	18	17.3358	2.75	47.67	20	6.5268	1.3	8.48	19	0.2136	0.37	2.2629	4.02	3.96	7.02
2	T9	A	6-Jun-94	18	13.1898	2.801	36.94	19	6.4527	2.363	15.25	18	0.2038	0.34	2.3048	3.37	4.03	5.41
2	T2	A	13-Jun-94	18	15.3928	2	30.79	14.9	5.8279	5.375	31.32	11.7	0.1597	0.87	1.6457	3.00	2.88	4.48
2	T6	A	13-Jun-94	18	17.3781	2.25	39.10	14.9	6.6022	7.3	48.20	12.4	0.1624	0.93	1.8514	3.53	3.24	5.73
2	T9	A	13-Jun-94	18	18.8074	2	37.61	14.9	3.9487	5.5	21.72	12.5	0.1628	1.00	1.6457	3.45	2.88	5.51
2	T2	A	21-Jun-94	18	16.948	2	33.90	19.6	6.4639	1.5	9.70	22.1	0.2276	0.28	1.6457	3.21	2.88	4.95
2	T6	A	21-Jun-94	18	16.9994	2	34.00	18.7	3.6986	2.1	7.77	17.8	0.2015	0.45	1.6457	3.22	2.88	4.96
2	T9	A	21-Jun-94	18	13.1518	2	26.30	16.8	3.1851	3.125	9.95	16.1	0.1852	0.47	1.6457	2.70	2.88	3.80
2	T2	A	27-Jun-94	18	13.2147	2	26.43	18.1	2.5087	1.5	3.76	18.7	0.2029	0.34	1.6457	2.71	2.88	3.82
2	T6	A	27-Jun-94	18	1.9367	2	3.87	17.7	1.5832	2.1	3.32	16.2	0.1896	0.06	1.6457	0.72	2.88	0.42
2	T9	A	27-Jun-94	18	13.7998	2	27.60	17.3	2.2286	3.125	6.96	15.6	0.1852	0.49	1.6457	2.79	2.88	4.00

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
2	T2	A	7-Jul-94	18	7.3721	2.125	15.67	15.2	3.7952	1.75	6.64	13.5	0.1678	0.36	1.7486	1.88	3.06	2.20
2	T6	A	7-Jul-94	18	17.8604	2	35.72	15.5	2.6791	1.475	3.95	13.6	0.1694	0.85	1.6457	3.33	2.88	5.22
2	T9	A	7-Jul-94	18	17.0454	2	34.09	15.5	2.7784	3.25	9.03	13.4	0.1686	0.82	1.6457	3.22	2.88	4.98
2	T2	A	11-Jul-94	18	12.0156	2.375	28.54	16.4	4.0061	2.375	9.51	15.7	0.1817	0.46	1.9543	2.84	3.42	4.14
2	T6	A	11-Jul-94	18	21.5466	2	43.09	16.5	6.9366	1.375	9.54	16.3	0.1847	0.77	1.6457	3.79	2.88	6.33
2	T9	A	11-Jul-94	18	11.8231	2	23.65	16.3	3.2702	3.5	11.45	15.7	0.1813	0.45	1.6457	2.51	2.88	3.40
2	T2	A	18-Jul-94	18	15.1116	2	30.22	20.6	5.0424	1.75	8.82	18.4	0.2136	0.32	1.6457	2.97	2.88	4.39
2	T6	A	18-Jul-94	18	14.7128	2	29.43	19.7	3.8838	0.875	3.40	18.3	0.2087	0.34	1.6457	2.91	2.88	4.27
2	T9	A	18-Jul-94	18	16.0776	1.875	30.15	17.7	5.142	1.125	5.78	16	0.1887	0.54	1.5429	2.97	2.70	4.38
2	T2	A	25-Jul-94	18	12.8113	2	25.62	21.5	4.1019	0.775	3.18	18.5	0.2187	0.25	1.6457	2.65	2.88	3.70
2	T6	A	25-Jul-94	18	13.7628	2	27.53	20.6	2.8644	0.5	1.43	17	0.2067	0.33	1.6457	2.78	2.88	3.99
2	T9	A	25-Jul-94	18	14.8072	2	29.61	20.3	2.8107	0.5	1.41	15.1	0.1963	0.43	1.6457	2.93	2.88	4.30
2	T2	A	2-Aug-94	18	14.6295	2	29.26	22.1	4.757	0.9	4.28	19.8	0.2287	0.24	1.6457	2.90	2.88	4.25
2	T6	A	2-Aug-94	18	11.4765	2	22.95	21.8	2.6203	0.5	1.31	18	0.2177	0.23	1.6457	2.46	2.88	3.30
2	T9	A	2-Aug-94	18	12.3771	2	24.75	21.8	0.9703	0.5	0.49	17.7	0.2162	0.25	1.6457	2.59	2.88	3.57
2	T2	A	8-Aug-94	18	12.7	1.975	25.08	19.4	3.0191	1.05	3.17	14.5	0.1896	0.42	1.6251	2.61	2.84	3.62
2	T6	A	8-Aug-94	18	12.9667	2	25.93	11.1	1.6692	1.05	1.75	13.4	0.1521	0.84	1.6457	2.67	2.88	3.75
2	T9	A	8-Aug-94	18	13.869	1.95	27.04	19.5	0.4125	0.925	0.38	12.4	0.1809	0.53	1.6046	2.75	2.81	3.91
2	T2	A	15-Aug-94	18	13.8565	1.975	27.37	20.9	4.3822	1.05	4.60	19.5	0.2208	0.26	1.6251	2.77	2.84	3.96
2	T6	A	15-Aug-94	18	15.5004	2	31.00	20.8	0.9203	1.05	0.97	18.8	0.2167	0.31	1.6457	3.02	2.88	4.51
2	T9	A	15-Aug-94	18	14.6707	1.95	28.61	19.9	-0.001	0.925	0.00	17.3	0.2048	0.37	1.6046	2.86	2.81	4.15
2	T2	A	22-Aug-94	18	13.5016	1.95	26.33	21	4.8461	1	4.85	20.5	0.2265	0.23	1.6046	2.70	2.81	3.81
2	T6	A	22-Aug-94	18	14.0275	1.525	21.39	20.4	0.7324	1	0.73	19.3	0.2172	0.28	1.2549	2.36	2.20	3.06
2	T9	A	22-Aug-94	18	13.283	2	26.57	20.3	1.2553	0.9	1.13	17.4	0.2072	0.32	1.6457	2.72	2.88	3.84
2	T2	A	29-Aug-94	18	13.2469	1.955	25.90	18.4	4.8631	0.95	4.62	15.3	0.1887	0.44	1.6087	2.67	2.82	3.74
2	T6	A	29-Aug-94	18	11.7405	2	23.48	17.4	0.1282	0.64	0.08	13.2	0.1754	0.50	1.6457	2.49	2.88	3.38
2	T9	A	29-Aug-94	18	13.7284	2	27.46	17.4	0.1575	1.028	0.16	11.8	0.1698	0.65	1.6457	2.78	2.88	3.98
2	T2	A	5-Sep-94	18	14.0436	1.862	26.15	18	2.1054	1.128	2.37	15.5	0.1878	0.48	1.5322	2.69	2.68	3.78
2	T6	A	5-Sep-94	18	13.9024	2	27.80	17.5	0.0235	1.056	0.02	14	0.1792	0.55	1.6457	2.80	2.88	4.03
2	T9	A	5-Sep-94	18	13.085	2	26.17	16.4	0.2555	1.432	0.37	10.9	0.1624	0.70	1.6457	2.69	2.88	3.78
2	T2	A	12-Sep-94	18	14.9329	2	29.87	13.1	4.5965	3.08	14.16	10	0.1472	1.06	1.6457	2.94	2.88	4.34
2	T6	A	12-Sep-94	18	14.9962	1.882	28.22	13.2	1.2597	2.75	3.46		0.1590	0.86	1.5486	2.84	2.71	4.09
2	T9	A	12-Sep-94	18	13.9505	2	27.90	13.5	4.0957	3.143	12.87	10.8	0.1514	0.91	1.6457	2.81	2.88	4.04
2	T2	A	19-Sep-94	18	18.3101	1.882	34.46	17.1	4.7814	1.672	7.99	13.2	0.1742	0.80	1.5486	3.25	2.71	5.03
2	T6	A	19-Sep-94	18	20.5402	2	41.08	16.4	2.3672	4.539	10.74	12.2	0.1674	1.01	1.6457	3.66	2.88	6.03
2	T9	A	19-Sep-94	18	14.3752	2	28.75	15.8	3.7272	1.943	7.24	11.7	0.1632	0.76	1.6457	2.87	2.88	4.17
2	T2	A	26-Sep-94	18	14.7892	1.882	27.83	13.9	3.0982	1.597	4.95	9.5	0.1482	1.03	1.5486	2.81	2.71	4.03
2	T6	A	26-Sep-94	18	15.8262	1.938	30.67	14.2	3.1736	11.25	35.70	9.7	0.1499	1.06	1.5947	3.00	2.79	4.46
2	T9	A	26-Sep-94	18	16.2001	2	32.40	13.9	3.5365	2.154	7.62	10.5	0.1517	1.06	1.6457	3.11	2.88	4.72

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
			Min		1.9367	1.525	3.8734	11.1	-0.001	0	-0.0009	9.5	0.1472	0.06	1.2549	0.72	2.20	0.42
			Median		14.5024	2	28.5725	17.7	3.40335	1.4875	4.89696	15.5	0.1850	0.47	1.6457	2.85	2.88	4.14
			Max		21.5466	6.144	106.727	22.1	10.8646	11.25	51.7155	22.1	0.2292	1.06	5.0556	6.81	8.85	15.92
			Mean		14.5739	2.255944	32.88	17.7235294	3.65689	2.1455	7.85	15.254717	0.1858	0.57	1.8563	3.10	3.25	4.88
			SD		2.96299	0.927078	2.75	2.72312969	2.4649	1.971066	4.86	3.20987455	0.0250	0.29	0.7629	0.98	1.33	2.70
			n		54	54	2916.00	51	54	54	2916.00	53	54.0000	54.00	54.0000	54.00	54.00	54.00
3	T3	A	1-Jul-92	18	0.0082	2	0.02	20.6	0.00095	2.031871	0.00	21	0.2292	0.00	1.6457	0.02	2.88	-0.16
3	T5	A	1-Jul-92	18	0.0082	2	0.02		0.00068	2.031871	0.00		0.0338	0.00	1.6457	0.02	2.88	-0.16
3	T7	A	1-Jul-92	18	0.0082	2	0.02		0.00089	2.031871	0.00		0.0338	0.00	1.6457	0.02	2.88	-0.16
3	T3	A	16-Jul-92	18	0.0157	2	0.03	19	3.7E-05	2	0.00	16.2	0.1830	0.00	1.6457	0.03	2.88	-0.16
3	T5	A	16-Jul-92	18	0.0157	1.765	0.03	18.5	4.3E-05	1.765	0.00	16.8	0.1882	0.00	1.4523	0.02	2.54	-0.16
3	T7	A	16-Jul-92	18	0.0157	2.308	0.04	18.4	1.8E-05	2.143	0.00	16.8	0.1882	0.00	1.8992	0.03	3.32	-0.16
3	T3	A	20-Jul-92	18		1.034		19.8		0.17		19.2						
3	T5	A	20-Jul-92	18		1.304		18.8		0.556		19.7						
3	T7	A	20-Jul-92	18		1.304		18.5		0.536		18.4						
3	T3	A	22-Jul-92	18		2.5		22.8		1.154		17.6						
3	T5	A	22-Jul-92	18		1.765		22		1.765		17.7						
3	T7	A	22-Jul-92	18		2		21.3		1.111		17.4						
3	T3	A	1-Aug-92	18	0.00832	1.899	0.02	20.1	7.6E-05	1.413	0.00	19.9	0.2177	0.00	1.5626	0.02	2.73	-0.16
3	T5	A	1-Aug-92	18	0.00832	2.893	0.02	20.1	0.00087	1.875	0.00	19.7	0.2156	0.00	2.3805	0.02	4.17	-0.16
3	T7	A	1-Aug-92	18	0.00832	2.4165	0.02	19.7	0.00042	1.881	0.00	18.8	0.2067	0.00	1.9884	0.02	3.48	-0.16
3	T3	A	17-Aug-92	18		1.899		20.3		1.413		13.3						
3	T5	A	17-Aug-92	18		2.893		19.7		1.875		13.4						
3	T7	A	17-Aug-92	18		2.4165		19.8		1.881		13.3						
3	T3	A	23-Aug-92	18		2.143		14.6		1.429								
3	T5	A	23-Aug-92	18		2.308		14		1.579		11.1						
3	T7	A	23-Aug-92	18		2.722		13.7		1.875		10.9						
3	T3	A	2-Sep-92	18		1.667		14.7		4.286		14.6						
3	T5	A	2-Sep-92	18		1.364		14.3		1.2		14.2						
3	T7	A	2-Sep-92	18		1.304		13.9		3.75		12.8						
3	T3	A	3-Sep-92	18		2		12.5		1.875		8.7						
3	T5	A	3-Sep-92	18		1.875		12.3		1.5		9.1						
3	T7	A	3-Sep-92	18		1.667		12.2		1.304		9						
3	T3	A	8-Sep-92	18		1.579		11.6		4.286		7.2						
3	T5	A	8-Sep-92	18		1.667		11.5		3.75		11.5						
3	T7	A	8-Sep-92	18		1.765		11.1		5		7.1						
3	T3	A	10-Sep-92	18		2.727		14.2		2.5		10.2						
3	T5	A	10-Sep-92	18		2.5		13.1		2.308		10.4						
3	T7	A	10-Sep-92	18		2.5		12.9		2.5		9.3						

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
3	T3	A	26-Sep-92	18		1.765		4.2		2.308		5.2						
3	T5	A	26-Sep-92	18		2		5.9		2		5.9						
3	T7	A	26-Sep-92	18		2		4.6		2.143		5.6						
			min		0.0082	1.034	0.0158	4.2	1.8E-05	0.17	3.9E-05	5.2	0.0338	0.00	1.4523	0.02	2.54	-0.16
			median		0.00832	2	0.02011	14.65	0.00042	1.878	0.00078	13.3	0.1882	0.00	1.6457	0.02	2.88	-0.16
			max		0.0157	2.893	0.03624	22.8	0.00095	5	0.00193	21	0.2292	0.00	2.3805	0.03	4.17	-0.16
			Mean		**0.01074**	**1.998529**	**0.02272**	**16.25825**	**0.00044**	**2.031871**	**0.00087**	**13.8870968**	**0.1663**	**0.00**	**1.7629**	**0.02**	**3.09**	**-0.16**
			SD		**0.00372**	**0.477033**	**0.00758**	**4.241115**	**0.00041**	**1.074593**	**0.00082**	**4.47919204**	**0.0767**	**0.00**	**0.2834**	**0.00**	**0.50**	**0.00**
			n		**9**	**34**	**9**	**32**	**9**	**34**	**9**	**31**	**9.0000**	**9.00**	**9.0000**	**9.00**	**9.00**	**9.00**
3	T3	A	21-Jun-93	6		0		16.1		0		15.2						
3	T5	A	21-Jun-93	6		9.465		16.2		0		16.5						
3	T7	A	21-Jun-93	6		11.625		16.2		11.125		17						
3	T3	A	28-Jun-93	6	0.01348	5.5	0.07	15.6	0.00932	5	0.05	14.7	0.1706	0.00	4.5257	0.05	7.92	-0.15
3	T5	A	28-Jun-93	6	0.01536	7.5	0.12	15.3	0.01076	5.5	0.06	14	0.1651	0.01	6.1714	0.06	10.80	-0.14
3	T7	A	28-Jun-93	6	0.01828	8.25	0.15	15.2	0.01268	7.25	0.09	14.2	0.1666	0.01	6.7886	0.07	11.88	-0.14
3	T3	A	4-Jul-93	6	0.01232	7.75	0.10	17.6	0.01176	4.375	0.05	23	0.2517	0.00	6.3771	0.05	11.16	-0.15
3	T5	A	4-Jul-93	6	0.0176	6.125	0.11	17.5	0.01088	5.25	0.06	22.6	0.2471	0.00	5.0400	0.06	8.82	-0.14
3	T7	A	4-Jul-93	6	0.01204	6.375	0.08	17.6	0.01216	5.75	0.07	22.9	0.2506	0.00	5.2457	0.05	9.18	-0.15
3	T3	A	9-Jul-93	6		7.75		14.8		4.375		15.5						
3	T5	A	9-Jul-93	6		6.125		14.9		5.25		13.8						
3	T7	A	9-Jul-93	6		6.375		14.8		5.75		13.3						
3	T3	A	13-Jul-93	6	0.01028	5.625	0.06	15.6	0.01592	4.875	0.08	15.2	0.1746	0.00	4.6286	0.04	8.10	-0.15
3	T5	A	13-Jul-93	6	0.01198	6	0.07	15.8	0.008	6	0.05	17.6	0.1954	0.00	4.9371	0.04	8.64	-0.15
3	T7	A	13-Jul-93	6	0.02444	6	0.15	15.8	0.00916	4.75	0.04	18.8	0.2067	0.01	4.9371	0.07	8.64	-0.14
3	T3	A	19-Jul-93	6	0.01436	6	0.09	18.2	0.011	5.75	0.06	14.3	0.1674	0.01	4.9371	0.05	8.64	-0.15
3	T5	A	19-Jul-93	6	0.00532	6	0.03	18.2	0.01004	4.5	0.05	15.7	0.1788	0.00	4.9371	0.03	8.64	-0.16
3	T7	A	19-Jul-93	6	0.01052	6	0.06	18.4	0.0118	6	0.07	18.3	0.2019	0.00	4.9371	0.04	8.64	-0.15
3	T3	A	27-Jul-93	6	0.01524	5.5	0.08	18.9	0.00916	6.25	0.06	16.4	0.1847	0.01	4.5257	0.05	7.92	-0.15
3	T5	A	27-Jul-93	6	0.011	6.25	0.07	19.6	0.00884	5.25	0.05	18	0.1991	0.00	5.1429	0.04	9.00	-0.15
3	T7	A	27-Jul-93	6	0.01244	6	0.07	19.9	0.01244	6.5	0.08	21.4	0.2335	0.00	4.9371	0.05	8.64	-0.15
3	T3	A	3-Aug-93	6	0.01384	5	0.07	17.5	0.00852	4.625	0.04	22.8	0.2494	0.00	4.1143	0.04	7.20	-0.15
3	T5	A	3-Aug-93	6	0.01112	6	0.07	17.3	0.00894	2.5	0.02	21.7	0.2368	0.00	4.9371	0.04	8.64	-0.15
3	T7	A	3-Aug-93	6	0.01368	6	0.08	17.3	0.01172	4.5	0.05	20.3	0.2218	0.00	4.9371	0.05	8.64	-0.15
3	T3	A	9-Aug-93	6	0.01328	7	0.09	17.6		6		15.1	0.1738	0.00	5.7600	0.05	10.08	-0.15
3	T5	A	9-Aug-93	6	0.00585	3	0.02	17.6	0.00684	2.75	0.02	15.2	0.1746	0.00	2.4686	0.02	4.32	-0.16
3	T7	A	9-Aug-93	6	0.01504	6	0.09	17.7	0.0196	5.5	0.11	14.5	0.1690	0.01	4.9371	0.05	8.64	-0.15
3	T3	A	16-Aug-93	6	0.0176	4.5	0.08	16.9	0.0128	5	0.06	19.6	0.2146	0.00	3.7029	0.05	6.48	-0.15
3	T5	A	16-Aug-93	6	0.01276	3	0.04	16.6	0.00828	2.625	0.02	18.9	0.2077	0.00	2.4686	0.03	4.32	-0.15
3	T7	A	16-Aug-93	6	0.0112	6	0.07	16.3	0.00928	5.75	0.05	13.7	0.1628	0.00	4.9371	0.04	8.64	-0.15

Appendix I.2 Predicted Results from the Three Model

					Inflow Paramters				Outflow Parameters									
Treatment	Trench	Station	Date	HRT (d)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	NH4 (mg/L)	Flow (L/min)	Load (mg/min)	Temperature (°C)	Kt	model 1	HLR	model 2	Flow (m^3/d)	model 3
3	T3	A	23-Aug-93	6	0.0126	7	0.09	19.5	0.00824	6	0.05	17	0.1900	0.00	5.7600	0.05	10.08	-0.15
3	T5	A	23-Aug-93	6	0.018	3	0.05	19.1	0.00964	1.25	0.01	15.3	0.1754	0.01	2.4686	0.04	4.32	-0.15
3	T7	A	23-Aug-93	6	0.01416	6	0.08	19	0.01076	4.875	0.05	14.2	0.1666	0.01	4.9371	0.05	8.64	-0.15
3	T3	A	30-Aug-93	6	0.01272	7	0.09	14.4	0.01204	6.125	0.07	14.4	0.1682	0.00	5.7600	0.05	10.08	-0.15
3	T5	A	30-Aug-93	6	0.01192	3	0.04	14.7	0.01356	0	0.00	14.8	0.1714	0.00	2.4686	0.03	4.32	-0.16
3	T7	A	30-Aug-93	6	0.01348	6	0.08	14.2	0.00904	4.875	0.04	13	0.1575	0.01	4.9371	0.05	8.64	-0.15
3	T3	A	7-Sep-93	6	0.0196	7	0.14	13.3	0.009	6.25	0.06	10.1	0.1375	0.01	5.7600	0.07	10.08	-0.14
3	T5	A	7-Sep-93	6	0.01416	0	0.00	8.7	0.00888			9.4	0.1257	0.01	0.0000		0.00	
3	T7	A	7-Sep-93	6	0.01492	6	0.09	14.2	0.01328	5	0.07	13	0.1575	0.01	4.9371	0.05	8.64	-0.15
3	T3	A	13-Sep-93	6	0.0128			10.4	0.01108			7.5	0.0964	0.01	0.0000		0.00	
3	T5	A	13-Sep-93	6	0.00492			3.6	0.01084			6	0.0782	0.00	0.0000		0.00	
3	T7	A	13-Sep-93	6	0.01504			10.3	0.00848			5.1	0.0689	0.01	0.0000		0.00	
3	T3	A	20-Sep-93	6	0.014			10.8	0.00872			9.3	0.1240	0.01	0.0000		0.00	
3	T5	A	20-Sep-93	6	0.01476			5	0.00492			7.7	0.0991	0.01	0.0000		0.00	
3	T7	A	20-Sep-93	6	0.01384			11.4	0.01056			5.9	0.0771	0.01	0.0000		0.00	
3	T3	A	27-Sep-93	6	0.0143			8.2	0.01136			7.3	0.0937	0.01	0.0000		0.00	
3	T5	A	27-Sep-93	6	0.01472			5.2	0.0102			6.3	0.0815	0.01	0.0000		0.00	
3	T7	A	27-Sep-93	6	0.01292			8.3	0.00852			6.4	0.0827	0.01	0.0000		0.00	
3	T3	A	4-Oct-93	6				4.3				4.4						
3	T5	A	4-Oct-93	6				4				4.9						
3	T7	A	4-Oct-93	6				4.1				4.1						
3	T3	A	12-Oct-93	6				1.2				4						
3	T5	A	12-Oct-93	6				1.4				5.2						
3	T7	A	12-Oct-93	6				1				4.2						
			Min		0.00492	0	0	1	0.00492	0	0	4	0.0689	0.00	0.0000	0.02	0.00	-0.16
			Median		0.01358	6	0.0792	15.6	0.0102	5.125	0.05274	14.45	0.1710	0.00	4.9371	0.05	8.64	-0.15
			Max		0.02444	11.625	0.15081	19.9	0.0196	11.125	0.1078	23	0.2517	0.01	6.7886	0.07	11.88	-0.14
			Mean		**0.21753**	**6.394928**	**0.33071**	**14.2063169**	**0.21929**	**5.45499**	**0.32256**	**13.995911**	**0.3666**	**0.21**	**3.6964**	**0.31**	**6.32**	**0.12**
			SD		**1.3548**	**4.953429**	**1.50885**	**5.60967365**	**1.37093**	**5.093564**	**1.55794**	**5.99007809**	**1.3328**	**1.36**	**2.4164**	**1.54**	**4.00**	**1.57**
			n		**44**	**41**	**35**	**54**	**43**	**40**	**33**	**54**	**44.0000**	**44.00**	**44.0000**	**34.00**	**44.00**	**34.00**